BIO-SORPTION OF HEAVY METALS FROM WASTEWATER BY USING MARINE BIOMASS WASTES

by

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A thesis submitted to the
School of Graduate Studies
in partial fulfillment of the
requirements for the degree of
Master of Engineering

Faculty of Engineering and Applied Science
Memorial University of Newfoundland
May 2014

St. John's, Newfoundland Canada

Abstract

Significant advances in the waste treatment field during the last decade have conclusively shown the possibility of enhancing effluents' quality and wastewater solutions. Different techniques have been tested trying to remove impurities from polluted water with positive results. Among them, adsorption, a relatively new method, has proven to be a fast, economical, and universal method for treating wastewater laden with heavy metals [32]. The development of inexpensive and efficient sorbents has led to the rapid growth of research interest in the adsorption field, and as a result, several adsorbents have been tested with outstanding results.

The purpose of this study is to evaluate the ability of marine biomass, as an adsorbent, to remove heavy metals from aqueous solutions by comparing the absorption capacities at different values of pH, metal concentrations, and temperatures. Comparative adsorption studies of heavy metal ions are performed to investigate the uptake capacities of the biomass. Batch adsorption tests are performed at four different initial concentrations (20, 40, 60, 100 ppm), two different temperatures (273.5 and 298.15 K), and during 25 hours at four different values of pH (1, 3, 5, 7). All experiments are performed using heavy metal ion solutions (Cu, Pb, Zn, Fe and Ni).

Consequently, based on the results of the tests, it can be concluded that the marine biomass is a good bio-adsorbent for heavy metal removal from wastewater at standard conditions (room temperature) and at freezing conditions (0 °C). The analysis shows that the descending order of preference for adsorption of the different metallic ions is as follows: Pb > Fe > Zn > Cu > Ni at 0 °C. At room temperature, the analysis shows that the descending order of

preference for adsorption of the different metallic ions is as follows: Pb > Fe > Cu > Zn > Ni.

Additionally, based on the Kinetic analysis, we can conclude that for all the metals studied at most of the concentrations and pH values, the adsorption equilibrium is reached after 5 hours of contact time.

Key words: bio-adsorbents, chitin, heavy metals, lobster shells, pseudo-second order equation.

Acknowledgments

First, I would particularly like to thank Jessica Benkaroun for her personal support and great patience throughout, as always, for which my mere expression of gratitude and appreciation does not suffice. Thanks Jessica, the completion of this goal would not have been possible without your advice and sincere love.

Also, I would like to thank my parents, Arturo Valencia Arango and Irene Quintana Velasquez, for their endless support, love, enthusiasm, patience, and motivation throughout my career; it would not be possible to be at this stage of my professional career without them.

I would like to express my sincere gratitude to everybody that in a certain way have helped me to the conclusion of this important goal in my life; especially, I would like to express my grateful thanks to my supervisor, Dr. Shafiq Alam, for his guidance during the project, for his helpful suggestions, and for sharing with me his outstanding research experience.

Last but not least, I would like to thank to Moya Crocker for her support and assistance throughout my studies. Also, I would like to acknowledge the financial and academic support of Memorial University of Newfoundland; it has been a pleasure and also a privilege to spend a couple of years at this university.

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Nomenclature

1/n= Freundlich parameter related with the adsorption intensity

a_{ij}= competition coefficient between the adsorbate "i" and "j".

Al= aluminum

As= arsenic

b= constant related to the free energy of adsorption (Langmuir Isotherm model)

BTEX= benzene, toluene, ethylbenzene, and xylenes

Ce= equilibrium concentration

C_i = initial concentration of the metal in solution

C_f= final concentration of the metal in solution

CN= cyanide

Co= cobalt

CP= Cleaner production

Cr= chromium

Cu= cadmium

Cu= copper

DAF= Dissolved-Air Flotation

ED= Electrodialysis

Fe= iron

$(FeNi)_9S_8$= pentlandite

Hg= mercury

ICP-AES= Inductively Couple Atomic Emission Spectroscopy

ICP-OES= Inductively Coupled Plasma Optical Emission Spectrometry

K= Freundlich parameter related with the total adsorption capacity

ME= Membrane electrolysis

NF= nanofiltration

Ni= nickel

$(NiMg)_6Si_4O_{10}(OH)_8$= garnierite

NiS= millerite

ppm= part per million

P2= pollution prevention

Pb= lead

q_e= amount of solute adsorbed at equilibrium per unit weight of adsorbent [mg/g]

q_m= maximum adsorption capacity of the solute [mg/g]

q_{mi}= maximum amount of solute "i" adsorbed per unit weight of the adsorbent [mg/g]

Ra= radium

RO= reverse osmosis

rpm= revolutions per minute

SO_2= sulphur dioxide

TSM= Total suspended matter

TSS= Total Suspended Solids

UF= ultrafiltration

USEPA= United States Environmental Protection Agency

WCED= World Commission on Environmental and Development

Zn= zinc

Chapter 1

1. Introduction

According to the United Nations World Commission on Environmental and Development (WCED) in the Brundtland report, "Our Common Future," sustainability aims to meet present human needs without compromising the ability of future generations to meet their own needs [1]. In other words, sustainability entails using natural resources intelligently in order to preserve them for future generations. An intelligent use of natural resources implies the correct use and the application of knowledge to control natural resources in order to achieve a sustainable environment. Unfortunately, not everybody is aware of the importance of preserving natural resources, and as a result, there is a continuous deterioration of the ecological system and a reduction of natural resources.

Additionally, the absence of strict laws in developing countries plays an important role in the quality of the environment and people's health. Some companies in different industries emit thousands of pollutants into the environment without control, and hence more awareness and efficient processes need to be implemented in order to change or improve this situation.

For instance, the presence of heavy metals in ground water, soil, and air represents a risk for human health due to the characteristics of each metal. Metals, such as cadmium, nickel, copper, zinc, lead, arsenic, chromium, and thallium are widely known to be poisonous, with the exception of some metals that at low levels are indispensable to maintain the metabolism of

the human body. Nevertheless, at higher levels all heavy metals can lead to poisoning, representing a serious hazard to human health, fauna, and flora.

1.1 Problem statement

Numerous industries trying to minimize the impact of their activities on the environment encounter barriers, and as a consequence, water, land, and air are being polluted. For instance, mining firms encounter barriers in the implementation of cleaner technologies and strategies, and as a result, water sources are being contaminated with heavy metals, such as lead, copper, nickel, and zinc.

The most common barriers encountered by mining firms are economic and legislative.

- **Economic barrier**

Mining companies have found profitable benefits and fewer capital investments by using conventional techniques to reduce pollution from water sources rather than implementing cleaner and newer, but more expensive, technologies. Consequently, mining firms, especially "junior companies" with limited revenues and resources, invest more money in solving problems after wastes are produced than investing in technologies that prevent pollution. Thus economic barriers encountered by small companies with limited budgets increase pollution, and hence more techniques are being analyzed to remove pollutants from water, land, and air. This study will analyze one conventional technique by using biomass from marine wastes to try to remove some heavy metals from water sources.

- **Legislative barrier**

The main legislative barrier that industries encounter for treating wastes is the difficulty of adapting to new legislations that have to be followed. The economic weight of some industries in developed countries compared to developing countries can also make the legislation economically harder to follow [2]. According to Hilson, in his article, "Barriers to implementing cleaner technologies and cleaner production (CP) practices in the mining industry: a case study of the Americas," the major weakness of third world environmental legislations are "the lack of clear and continuous policies; the incomplete regulatory frameworks and uneven enforcement; the ignorance of characteristics of industrial production processes; and the inefficient coordination among different governmental agencies at different levels [2]. "

In conclusion, due to economic and legislative barriers, mining firms, especially small companies, are investing more in techniques to reduce pollution after waste is produced than in reducing pollution from its source before wastes are produced. This study will focus on reducing the water pollution caused by mining facilities in Newfoundland and Labrador, Canada.

Thus, the motivation of this study is to analyze the absorption of heavy metals from water sources by using alternatives derived from biomass. The purpose of using substitutes derived from biomass is to replace the current reagents and resins produced from petroleum that are detrimental to the environment. Additionally, it is important to note that although ion exchange resins and activated carbon have been recognized as effective methods for treating

wastewater, their low efficiency and high cost have limited their use in actual industrial scenarios [3].

1.2 Scope of the research

Research is being conducted on a variety of subjects to accomplish a common environmental goal: to reduce the amount of wastes before they are produced by preventing pollution in the effluent streams and to recover maximum amounts of pollutants after waste is produced from water sources by using separation techniques.

Consequently, several separation techniques have been used to recover heavy metals from aqueous solutions, such as chemical precipitation, evaporation, ion exchange, absorption, cementation electrolysis, and reverse osmosis. Some of them have proved to be effective but expensive at the same time; however, adsorption has emerged as a cheap and efficient solution that has been used by scientists during the last few years to recover metals from aqueous solutions.

This study will be focused on the bio-sorption of non-ferrous metals by using marine-based solid wastes found at low temperatures in mining facilities in Newfoundland and Canada. Specifically, we will be using the shells of lobsters to recover metals in aqueous media at 0 °C and at room temperature in order to determine how efficiently the reagent (bio-adsorbent produced with marine shells) absorbs non-ferrous metals.

1.3 Objective of research

There are a number of challenges in extractive metallurgy of non-ferrous metals and advanced materials. The greatest challenge involves the treatment of metallurgical wastewaters for product and by-product recovery and detoxification [4]. According to Bohumil Volesky, one of the pioneers in the bio-sorption field, three major points should be considered when choosing the metals for adsorption [5]:

1. The metal toxicity
2. Recovery interests
3. How representative is the metal in terms of its behaviour

The emphasis of this study will be based on the recovery of copper, zinc, lead, iron, and nickel from wastewater at low temperatures by using lobster biomass. Results have proven to be positive using crab biomass for temperatures ranging from 20 to 35 °C; however, no test has been performed to measure the recovery at low temperatures. Contaminated water sources are situated across Newfoundland and Labrador, especially close to mining facilities, where temperatures reach below 0 °C.

1.4 Thesis outline

This thesis consists of six chapters. The first chapter is the introduction chapter that shows the problem statement, scope, and objective of the research. The second chapter presents an introduction to the mining industry and its impact on the environment. Additionally, the

second chapter discusses a descriptive background of the mining industry in Newfoundland and Labrador followed by a detailed description of the heavy metals presented in waste-waters as a result of mining processes in Newfoundland and Labrador. The third chapter presents a complete characterization of chitin with its main industrial applications. The fourth chapter discusses the methods, materials, experiments, and the different techniques employed to characterize the efficiency of the marine biomass (shell of lobsters) recovering heavy metals from synthetic wastewater. The fifth chapter explains the results of the experiments used to verify the objective of this study. Finally, the sixth chapter shows the conclusions of the tests and also presents some limitations of this study.

Chapter 2

2. Background

2.1 Mining industry

Mining processes and activities are commonly known for their damage to the environment due to toxic wastes produced directly and indirectly. Traditionally, solutions for contaminated wastes were treated after they were produced; however, because of environmental regulations, solutions now focus on the treatment of wastes before they are created. The traditional view of managing wastes is also known as "end-of-pipe" because toxic or polluting substances receive treatment at the end of the production process. This approach usually transmits pollutants from one medium to another, and therefore the damage to the environment is only postponed [6].

Consequently, the establishment of environmental legislation has created the need for the mining industry to implement new and cleaner technologies to satisfy mandatory standards and to reduce the operative costs of treating wastes after they are produced. In other words, the application of new practices, such as pollution prevention and cleaner production have changed the mining industry's understanding of treating contaminated wastes before they are produced.

Glavic and Lukman, in their "Review of Sustainability Terms and their Definitions," define cleaner production as a systematically organized approach to production activities, which has positive effects on the environment. These activities "encompass resource use minimization,

improved eco-efficiency and source reduction in order to improve the environmental protection and to reduce risks to living organisms [6]." The successful implementation of these strategies not only reduces environmental conflicts, but also saves great quantities of money that would have been spent in clean-up processes [7].

According to Glavic and Lukman, the establishment of cleaner technologies implies the achievement of environmental improvements in process and product development through the correct and sustainable use of resources. Some of the management strategies used in cleaner technologies focus on increasing the efficiency of raw materials, improving energy efficiency and material flow management, implementing environmental approaches, and achieving environmental standards [6].

In the mining industry, the implementation of management strategies is quite significant because mining operations have a great impact on the environment; however, the awareness of mining damage was not realized until 1970, when the first legislation became active. Since the creation of environmental legislation "Circa-1970," the levels of pollution in the mining industry have been reduced considerably.

According to Hilson, in his article, "Pollution prevention and cleaner production in the mining industry: an analysis of current issues," the reduction in levels of pollution can be attributed to the implementation of three specific technologies: high-tech flue gas desulphurization (acid gas scrubbers), wastewater treatment technologies, and chemical detoxification [7].

1. High-tech flue gas desulphurization (acid gas scrubbers)

Most metals (ferrous and non-ferrous) occur naturally as sulfide compounds that, when in contact with chemicals, such as reducing substances, produce large quantities of sulphur dioxide. Sulphur dioxide (SO_2) is the main component of acid rain and its removal from soil and water requires spending significant quantities of money [7]. Mining operations emit significant quantities of sulphur dioxide into the environment as a result of smelting ferrous and non-ferrous metals. Consequently, mining companies have adopted desulphurization systems in order to reduce the emissions of SO_2 [7]. The latter technology is considered the only preventive and effective method of reducing the emissions of sulphur dioxide into the environment.

2. Wastewater treatment technologies

There are two major water pollutants in the mining industry. The first one is acid mine drainage and, according to Hilson, "since coal and most metals occur as sulphides, separating their deposits from uneconomic gangue creates vast quantities of waste rock and tailings, which if flushed with rainwater or snow-melt creates acid mine drainage [7]." The disposal of untreated acid mine drainage into water sources creates unfavorable conditions for sea life.

The second major pollutant in the mining industry comes from heavy metals, such as copper, lead, and arsenic that, when in contact with water, are leached and guided to rivers, lakes, and water sources. It is important to note that the purpose of this study is to analyze the removal of these heavy metals from water sources close to mining facilities at 0 °C. Low temperatures are commonly experienced for long periods of the year in northern zones of Canada.

The traditional methods used in the mining industry to solve end-of-pipe problems result in great clean-up costs for companies, and therefore firms have invested in the development of new technologies that notably reduce the pollution of water sources. According to Hilson, the most common technologies implemented by mining companies are [7]:

a. Electrochemical methods
b. Plasmotechnologies
c. Membrane filtration
d. Evaporation and crystallization
e. Biodegradation processes
f. Chemical precipitators

3. Chemical detoxification.

In the processes of extracting, leaching, and refining minerals, many toxic chemicals are used. The contact of chemicals with plants and animals has a negative impact on them, and mining companies need to prevent and control the deposition of chemicals into soil and water sources.

For instance, in the extraction of gold and silver, cyanide is used in a process called "Heap Leaching" to dissolve silver and gold particles. The result of the heap process leaves free metal cyanides, which cause lethal damage to a wide range of species when released into the environment. The same problems are caused when mining companies use other chemicals, such as Hg and surfactants.

Traditional methods that are used to clean chemicals have failed to prevent pollution, and as a result, some other strategies have been developed and implemented with better results. According to Hilson, some of the cleaner technologies implemented by mining companies in chemical detoxification are [7]:

g. Treatment of chemicals using hydrogen peroxide
h. SO_2/Air detoxification processes
i. Biological oxidation
j. Advanced chemical recycling
k. Catalysis, bio-oxidation and photolysis detoxification

Mining companies have spent thousands of dollars implementing new technologies that prevent water pollution, some of them with better results than others; however, some these technologies are not absolutely effective, and as a result, uncountable water sources are still being contaminated in mining operations. Thus, the analysis of this study will focus on the removal of heavy metals (non-ferrous metals) to solve end-of-pipe problems by using marine-based solid wastes at low temperatures in northern zones of Canada.

2.2 Mining industry in Canada

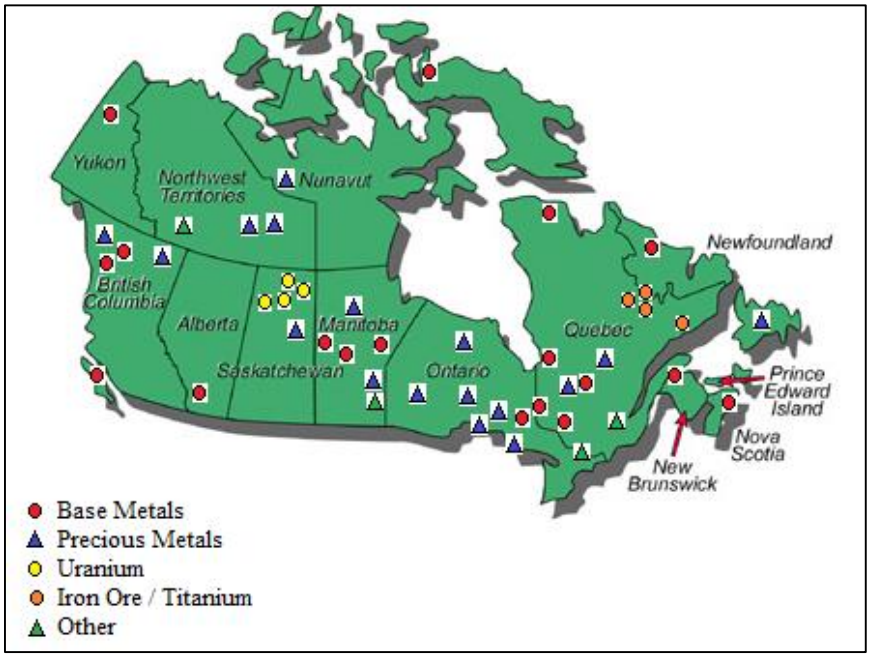
Metal mines in Canada are classified according to the primary commodity type in the following way:

- Base metals, such as copper, zinc, lead, and nickel
- Precious metals, such as gold, platinum, and silver

- Uranium
- Iron ore
- Other metals, such as titanium, tantalum, tungsten, niobium, and magnesium

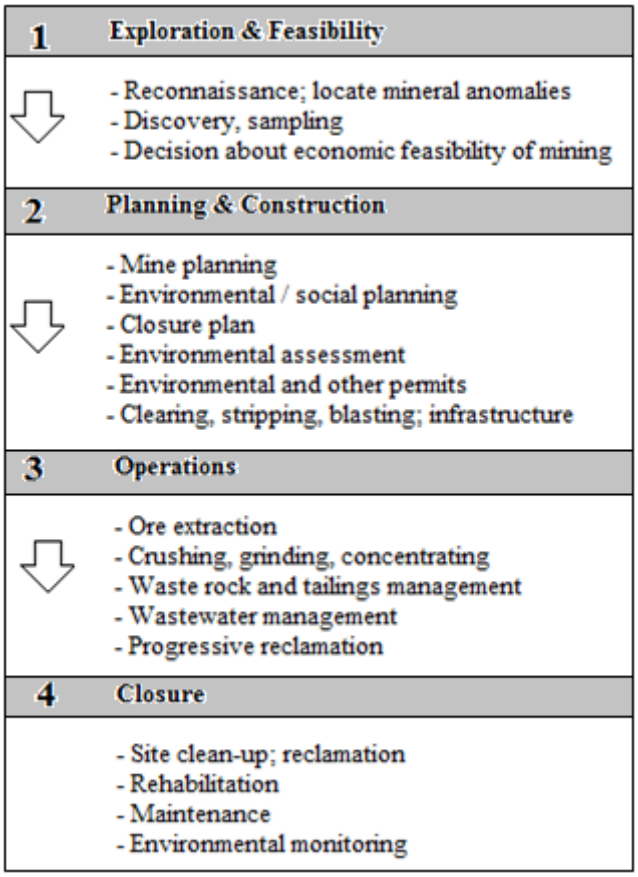
According to the Environmental Code of Practice for Metal Mines, the geographical distribution of the metal mines across Canada is presented in the Figure 2.1.

Figure 2.1. Distribution of mining facilities subject to the metal mining effluent regulations in Canada in 2007 [8]



In addition, in Canada, the life cycle of a typical mine involves the exploration and feasibility, planning and construction, operations, and closure phases. Figure 2.2 shows the main activities of a mine including activities performed at each stage of the life cycle.

Figure 2.2. Common activities of a mine life cycle [8]



Also, in Canada there is a code that is recommended to identify the best practices in order to achieve continual improvements in the environment; however, the procedures are not always followed according to the code, and as a consequence, the environment is affected.

According to the Environmental Code of Practice for Metal Mines in Canada, "water and wastewater management constitute the primary environmental concern at most metal mines in Canada [8]." Thus, an effective water management should include the following practices [8]:

1. Separation of clean and contaminated water flows in order to reduce the post-treatment of the effluent

2. Reduction of water usage
3. Recycling of water for different mining processes
4. Analysis of activities that may have an impact on the groundwater

In general, most of the measures are focused on reducing the flow on-site of water and preventing contaminated wastewaters leaving the mine; however, not all the procedures are followed according to the Environmental Code, and as a result, more and more water sources are being contaminated every day.

For instance, in 2011 toxic compounds, such as As, Cu, CN, Pb, Ni, Zn, and TSS were found exceeding the maximum authorized concentrations in effluents close to mining facilities. The number of exceedances in 2011 for 40 facilities across Canada was 74. Table 2.1 shows the number of exceedances and the number of facilities exceeding the authorized limits per toxic compound.

Table 2.1. Exceedances of limits per substance [9]

Substance / Parameter	Number of Excedances	Number of Facilities
Arsenic	2	2
Copper	1	1
Cyanide	1	1
Lead	0	0
Nickel	5	4
Zinc	4	3
TSS	53	22
Radium 226	1	1
pH	7	6
Total	**74**	**40**

Table 2.2. Compliance summary for deleterious substances and pH in 2011 [29]

	As	Cu	CN	Pb	Ni	Zn	TSS	Ra-226	pH Low	pH High
Number of exceedances	2	1	1	0	5	4	53	1	4	3
Total number of months for which results were reported	1203	1260	345	1 219	1209	1236	1346	832	1356	1356
Compliance Rate (%)	99.8	99.9	99.7	100	99.6	99.7	96.1	99.9	99.7	99.8

It is important to note that even though the compliance rate is more than 96% for each deleterious substance, environmental disturbance is still occurring, especially in aquatic ecosystems, due to exceedances in some toxic compounds. Thus, the need to select suitable methods for treating mining effluents is reasonably important. The number of exceedances and the compliance rate for each toxic compound present in mining facilities across Canada can be seen in Table 2.2.

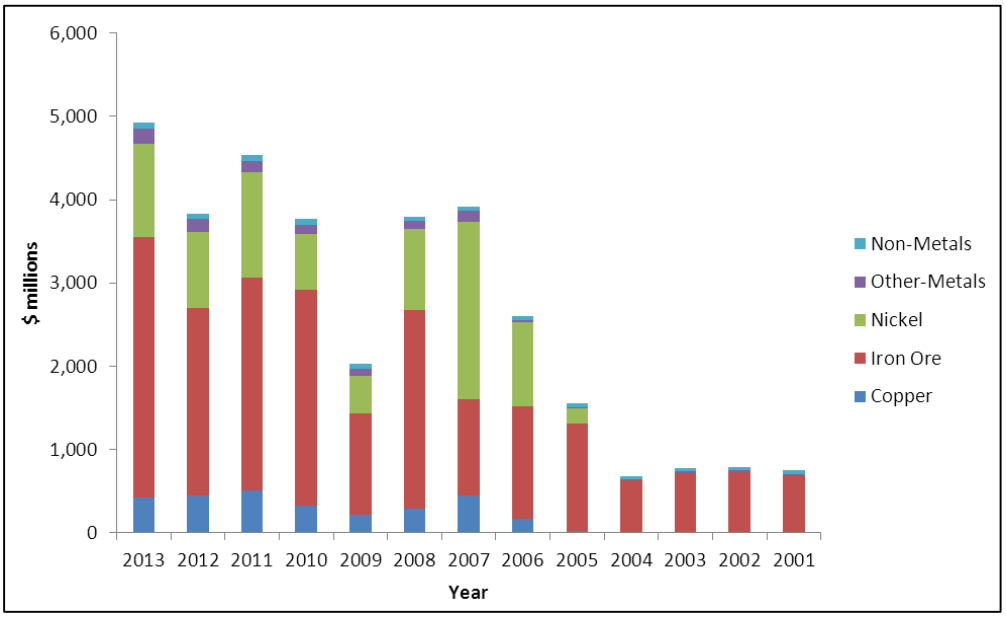
2.2.1 Newfoundland and Labrador mining industry

Mining is one of the largest industries in Newfoundland and Labrador and is considered a major contributor to the economy of the province. Newfoundland and Labrador has a diverse mineral industry that provides the world market with a wide range of commodities, such as iron, nickel, granite, slate, and limestone. Most of the commodities produced in the province go to the steel and construction industry.

According to the Department of Natural Resources, a total of 16 mineral commodities are being extracted or were extracted in the province. In 2012, 13 mines in total were operating in Newfoundland and Labrador, principally extracting iron ore, nickel, copper, zinc, cobalt, antimony, and gold. The mining industry has notably increased during the last ten years as a

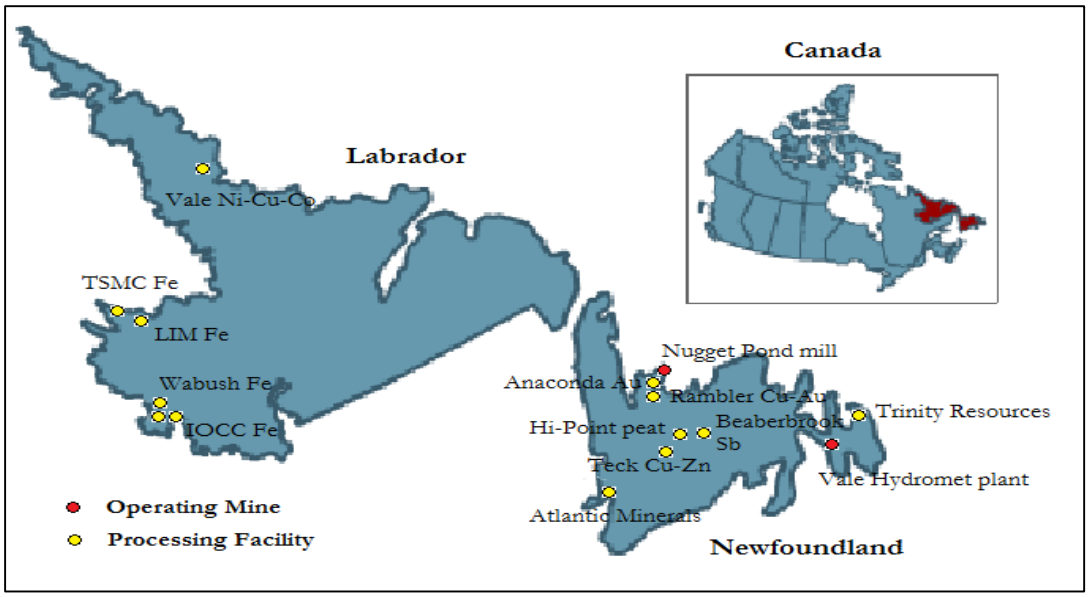
consequence of changes to processes, machinery, and the nature of the workforce. Figure 2.3 shows the increments on the gross value of mineral shipments in Newfoundland and Labrador since 2001. It is important to mention that for 2013, the gross value at the end of the year is estimated by the Department of Natural Resources in Canada.

Figure 2.3. Gross value of mineral shipments in Newfoundland and Labrador [10]



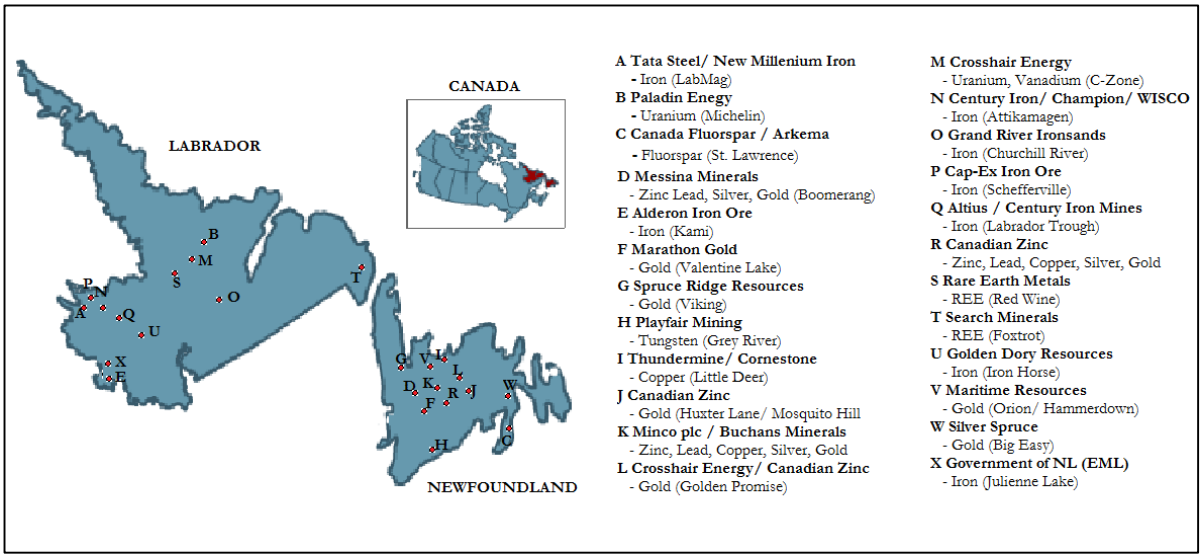
In Labrador are situated six metal mines extracting mostly nickel, copper, and iron. The other seven metal mines, located in Newfoundland, are focused on the extraction of metals, such as gold, copper, zinc, and antimony. Figure 2.4 shows the distribution in 2012 of the metal mines across Newfoundland and Labrador:

Figure 2.4: Newfoundland and Labrador mines in 2012 [10]



It is also important to mention that, in addition to the metal mines located in Newfoundland and Labrador, a large number of advanced projects and projects in development are in progress as a result of the mining expansion in the province during the last ten years. Some of these projects in Newfoundland and Labrador can be observed in Figure 5.

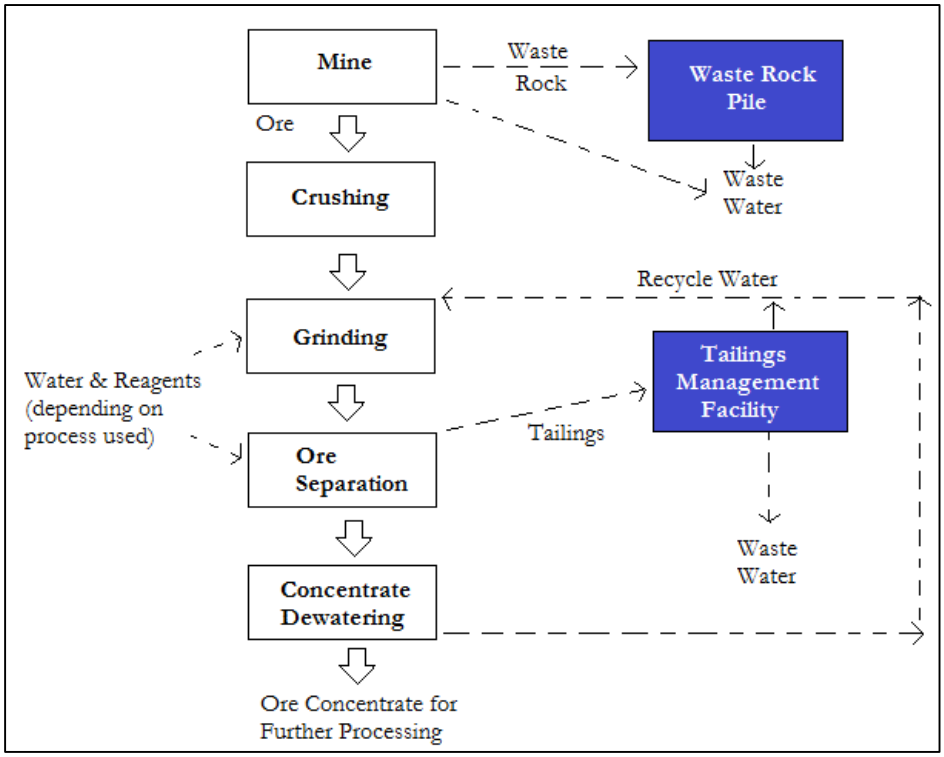
Figure 2.5. Projects in development in Newfoundland and Labrador [11]



Based on the actual number of mines in operation and projects in development in Newfoundland and Labrador, the provincial government of Newfoundland and Labrador has expressed its concern about the future environmental conditions of the province.

It is commonly known that, in mining processes, vast quantities of water are required, and as a consequence, water sources close to mining facilities are contaminated. Figure 2.6 shows the typical activities of a mine operation phase. According to the "Environmental Code of Practice for Metal Mines in Canada," "the operation phase represents the period during which a mine produces and processes ore to produce a product for market [8]." It is important to observe how significant water is during different mining activities, especially those activities related to the ore extraction.

Figure 2.6. Typical activities of the mine operations phase [8]



According to Gestring and Sumi, in their article, "Polluting the future: how mining companies are contaminating our nations in perpetuity," in the United States 17 to 27 billions of gallons of water are expected to be polluted every year in perpetuity by 40 existing gold, copper, and uranium mines [12]. The United States government highlights not only the cost to treat the water every year, but also the damage that is being done to the environment by mining industries.

Also, "in the midst of declining fresh water supplies, an increasing number of hard rock mining companies are generating water pollution that will last for hundreds or thousands of years and new projects are on the horizon [12]."

2.2.2 Potential sources of contamination

2.2.2.1 Acid mine drainage

Sulfide minerals are ore minerals for various base metals, such as copper, lead, and zinc that, in contact with water and oxygen, can oxidize to create sulfuric acid. This process is commonly known as acidic drainage and represents an important issue from an environmental perspective due to the hazard that it represents to the environment.

2.2.2.2 Alkaline effluents

In some mining processes, alkaline conditions are beneficial for ore separation practices, and as a result, chemicals are used to assure alkaline pH. It is quite common to find alkaline conditions in mining effluents, sometimes as high as pH 11; however, before waste-waters are discharged, they are treated to reduce its alkalinity. Alkaline conditions in discharge points

were present in most of the metal mines in Newfoundland and Labrador in 2001. Table 2.3 shows the effluent quality for metal mines in Newfoundland in 2001.

Table 2.3. Water pH in discharge points for metal mines in Newfoundland and Labrador in 2001 [13]

Mine Name	Company	Location	Discharge Point	pH
Iron Ore Company of Canada	Iron Ore Company of Canada	Labrador City	New Tailings Pump House	7.8
		Labrador City	Old Tailings Pump House	7.9
Scully	Wabush	Wabush	East Pit No.1 Dewatering	7.5
		Wabush	East Pit No.2 Settling Pond	7.1
		Wabush	West Pit No.5	7.0
		Wabush	South Pit	7.3

2.2.2.3 Metal Leaching

Water sources close to mining industries usually contain metals that naturally occur in the rock. Additionally, due to the fact that most of the metals are highly soluble in water at low values of pH, high concentrations of metals are found in water at low pH. Thus, concentrations of metals are usually elevated in acidic conditions; however, metal leaching also occurs in cases where acidic conditions are not presented in wastewater.

2.2.2.4 Cyanide and suspended solids

Cyanide is used in the recovery of gold, and as a result, wastewater from gold ores contains certain cyanide compounds. Also, another source of water pollution is the suspended solids that are classified as non-settleable and settleable. In the discharge process of effluents, high levels of solids can be in contact with aquatic ecosystems causing serious problems due to the lack of oxygen and reduced light.

2.2.3 Water pollution in Newfoundland and Labrador caused by the mining industry

Effluent quality for metal mines in Newfoundland and Labrador has changed throughout the years, especially after the expansion of the mining sector in the province. In 2001, the overall achievement of the monthly effluent quality standards in Atlantic regions was 97% with no exceedances of deleterious substances in metal effluents in the province; however, in 2011, more than 20 exceedances were reported in Newfoundland and Labrador in the summary review of performance of metal mines. The major problem causing the exceedances was attributed to TSM and zinc. The following table shows the annual average quality of the effluents for metal mines across Newfoundland and Labrador in 2001.

Table 2.4. Effluent quality for metal mines in Newfoundland and Labrador in 2001 [13]

Mine Name (Company) Location	Discharge Point	As	Cu	Ni	Pb	Zn	TSM	pH
		Metals and TSM in (mg/L)						
Iron Ore Company of Canada (Iron Ore Company of Canada) Labrador City	New Tailings Pump House	0.02	0.03	0.02	0.05	0.01	-	7.8
	Old Tailings Pump House	0.02	0.03	0.02	0.05	0.01	-	7.9
Scully (Wabush) Wabush	East Pit No.1 Dewatering	-	-	-	-	-	1.2	7.5
	East Pit No.2 Settling Pond	-	-	-	-	-	1.5	7.1
	West Pit No.5	-	-	-	-	-	6.4	7.0
	South Pit	-	-	-	-	-	6.5	7.3

It is significant to mention that the summary review of performance for metal mines uses data provided by mines on a quarterly and annual basis. The data is analyzed to compare the achievements of the mining industry every year.

It is also important to observe, based on Table 2.4, that most of the values of pH for each mine are higher than seven, which means that in 2001 most of the mines operating in Newfoundland and Labrador had no problems related to acid mine drainage; however, it is also essential to note that this situation nowadays have changed due to the mining expansion experienced in the province during the last ten years.

Table 2.5. Authorized limits of deleterious substances [14]

Deleterious Substance	Maximum Authorized Monthly mean Concentration (mg/L)
Arsenic	0.5
Copper	0.3
Cyanide	1.00
Lead	0.20
Nickel	0.50
Zinc	0.50
TSS (Total Suspended Solids)	15.00

Additionally, it is important to mention that based on the authorized limits of deleterious substances, all of the metals measured (As, Cu, Ni, Pb, Zn) in the effluent quality for metal mines in Newfoundland and Labrador in 2001 are below the authorized limits; however, it is important to clarify that the values exposed in Table 2.4 are values for 2001, when the mining industry was not as significant as it is now in terms of the number of projects in development and the number of mines operating. The maximum authorized limits of deleterious substances can be seen in Table 2.5.

Consequently, due to the mining expansion experienced during the last decade, the effluent quality for metal mines has notably changed in Newfoundland and Labrador. For instance, in

2011, 22 exceedances of limits for deleterious substances in Newfoundland and Labrador were reported. Among all the provinces in Canada, Newfoundland and Labrador had the second highest number of exceedances during 2011, following Quebec with a total of 24 exceedances during the same year. Table 2.6 shows the distribution of exceedances for various metals and suspended solids per province.

Table 2.6. Distribution of exceedances by jurisdiction in 2011 [9]

Jurisdiction	As	Cu	CN	Pb	Ni	Zn	TSS	Ra-226	pH	Total	Number of Facilities
British Columbia	-	-	-	-	-	-	2	-	1	**3**	2
Yukon	-	-	-	-	-	-	2	-	2	**4**	2
Saskatchewan	-	-	-	-	-	-	1	-	-	**1**	1
Manitoba	1	-	-	-	-	-	5	1	-	**7**	4
Northern Territories	-	-	-	-	-	-	-	-	-	**-**	-
Nunavut	-	-	-	-	-	-	-	-	-	**-**	-
Ontario	1	1	1	-	2	-	7	-	-	**12**	9
Quebec	-	-	-	-	3	3	15	-	3	**24**	11
New Brunswick	-	-	-	-	-	-	-	-	-	**-**	-
Newfoundland and Labrador	-	-	-	-	-	1	21	-	-	**22**	4
Nova Scotia	-	-	-	-	-	-	-	-	1	**1**	1
Total	**2**	**1**	**1**	**-**	**5**	**4**	**53**	**1**	**1**	**74**	**34**

It is important to mention that, based on the number of facilities in Newfoundland and Labrador, the number of exceedances is considerably high taking into account that Quebec has twice the facilities of Newfoundland and Labrador. Thus, due to the fact that numerous exceedances are being caused in the province every year, newer methods need to be implemented to treat and maintain the equilibrium of living ecosystems. Figures 2.7 and 2.8 show the number of facilities and the facilities with exceedances per province.

Figure 2.7. Number of facilities with exceedances per province in 2011 [9]

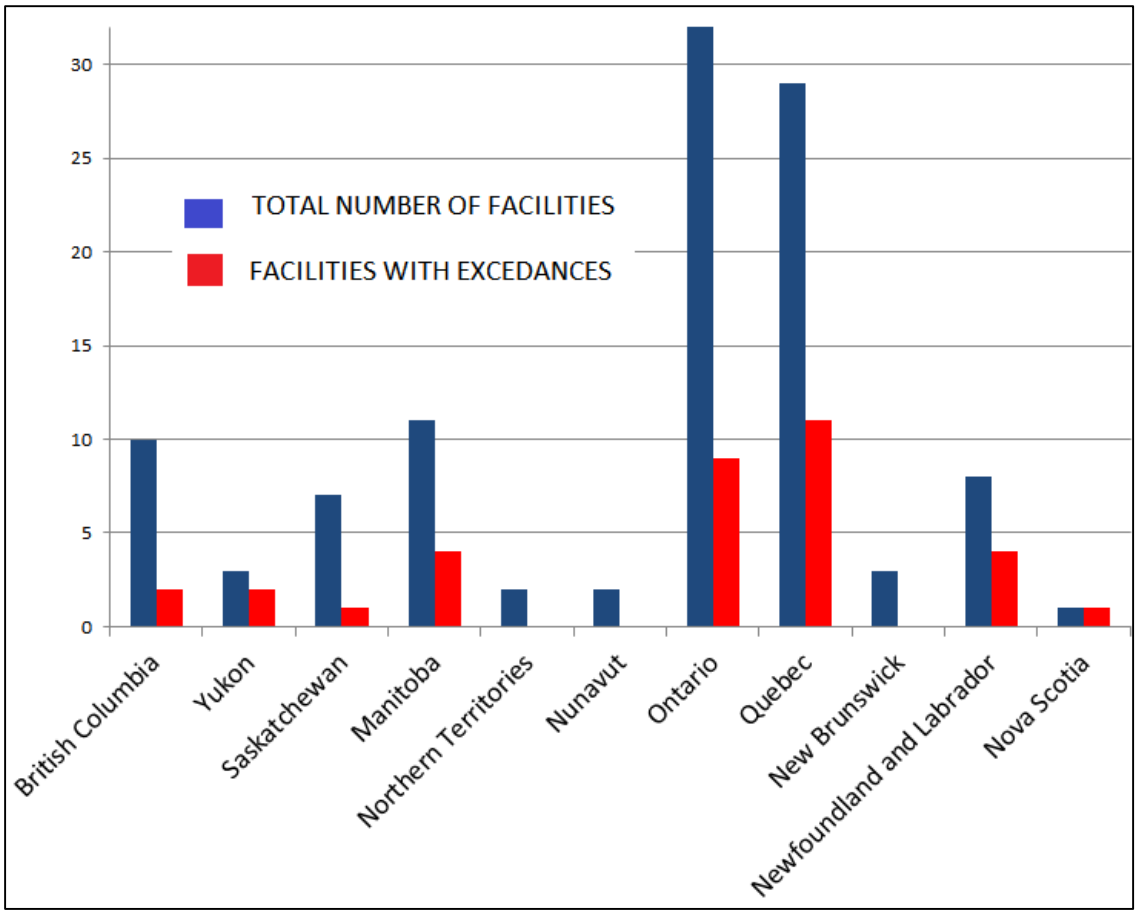
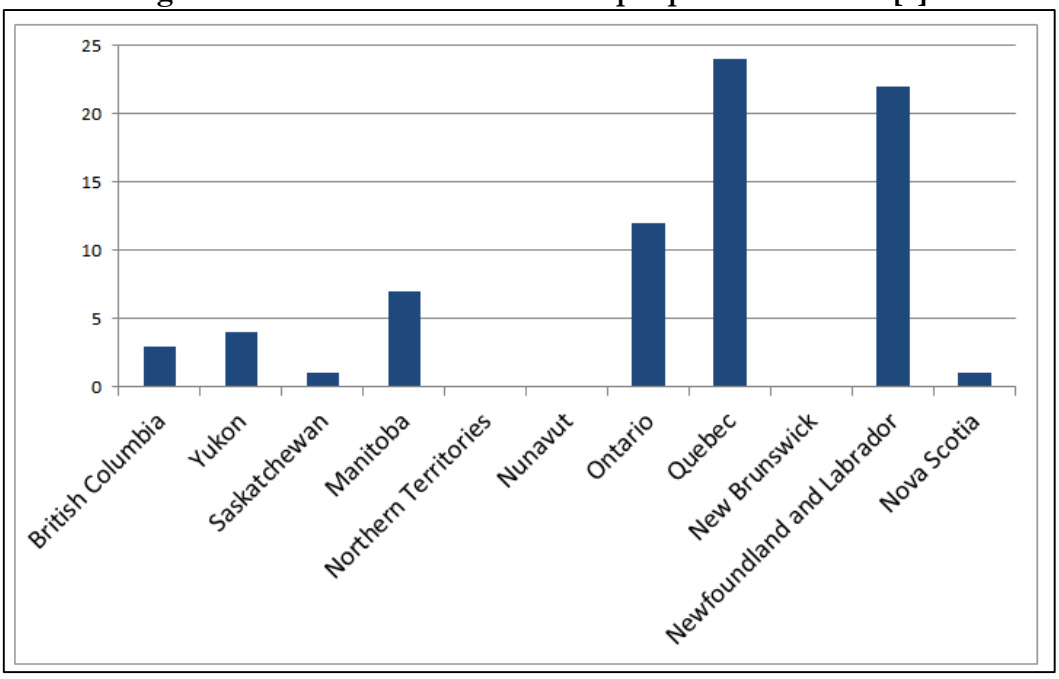


Figure 2.8. Number of exceedances per province in 2011 [9]



2.2.4 Contaminated water by the mining industry in Newfoundland and Labrador

According to the "Environmental Code of Practice for Metal Mines", an effective wastewater treatment is important to guarantee that mine effluents do not pollute aquatic ecosystems. Consequently, activities, such as the adjustment of water pH and the reduction of metals' concentrations, should be considered in treatment of wastewater in order to prevent water pollution.

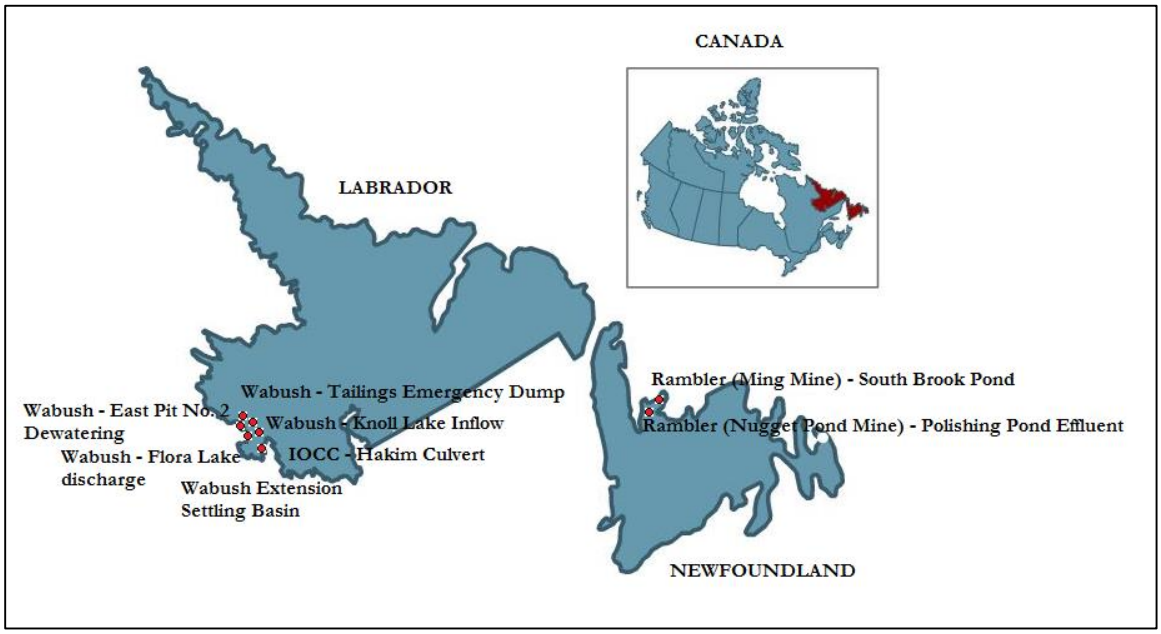
Nevertheless, wastewater treatment has not been quite effective, and as a result, more than 20 exceedances were presented in Newfoundland and Labrador in 2011. Wabush Mines, a company operating in Labrador since 1965, accounts for more than 15 exceedances in 2011 related to Total Suspended Solids (TSS). It is important to mention that although none of the exceedances caused in Labrador by Wabush Mines are related to heavy metals, the impact of suspended solids in discharge points is significant for quality control standards. The presence of suspended solids in discharge points notably impacts plant and aquatic life. The distribution of exceedances per company in Newfoundland and Labrador in 2011 can be seen in Table 2.7.

Table 2.7. Summary of Exceedances for mines in Newfoundland and Labrador in 2011 [9]

Company	Discharge Point	Number of Months of Discharge	As	Cu	Ni	Pb	Zn	TSS	pH
			Number of Exceedances						
Iron Ore Company of Canada	Hakim Culvert	12						1	
Ming Mine	South Brook Pond	6					1		
Nugget Pond Mine	Polishing Pond Effluent	11						1	
Wabush Mines joint Venture (Scully Mine)	East Pit No. 2 Dewatering	12						3	
Wabush Mines joint Venture (Scully Mine)	Flora Lake Discharge	12						1	
Wabush Mines joint Venture (Scully Mine)	Knoll Lake Inflow	12						10	
Wabush Mines joint Venture (Scully Mine)	Tailings Line Emergency Dump	5						4	
Wabush Mines joint Venture (Scully Mine)	West Pit Extension Settling Basin	12						1	

According to the Department of Environment and Conservation in Canada, in 2012, mining companies, such as Anaconda Mining Inc. and Rambler Metals, reported exceedances in cyanide and zinc, respectively. Beaver Brook Antimony Mine, Iron Ore Company of Canada, and Labrador Iron Mines reported exceedances in total suspended solid [15]. Figure 9 shows the location of the exceedances across Newfoundland and Labrador in 2012.

Figure 2.9. Location of the exceedances across Newfoundland and Labrador in 2012 [15]



It is important to observe that, although the compliance rate is more than 96% for each deleterious substance, environmental disturbance is still occurring, and as a consequence, diverse methods have been tested to treat wastewater. Among them, bio-sorption has emerged as an economical and efficient method to treat wastewater laden with heavy metals.

2.3 Water Pollution

According to the "Environmental Quality Act of 1974", pollution is defined as "any direct or indirect alteration of the physical, thermal, chemical, or biological properties of any part of the environment by discharging, emitting, or depositing environmentally hazardous substances, pollutants or wastes [16]." Based on the definition of pollution by the "Environmental Quality Act of 1974", water pollution can be defined as a change in the chemical, physical, and biological quality of water that is harmful to public health, animals, birds, wildlife, fish or aquatic life. It is important to note that this definition of water pollution is based on the fact that any change in water quality is induced by human intervention. In other words, the discharge, dispose, or release of toxic materials from mining facilities in water sources is considered pollution.

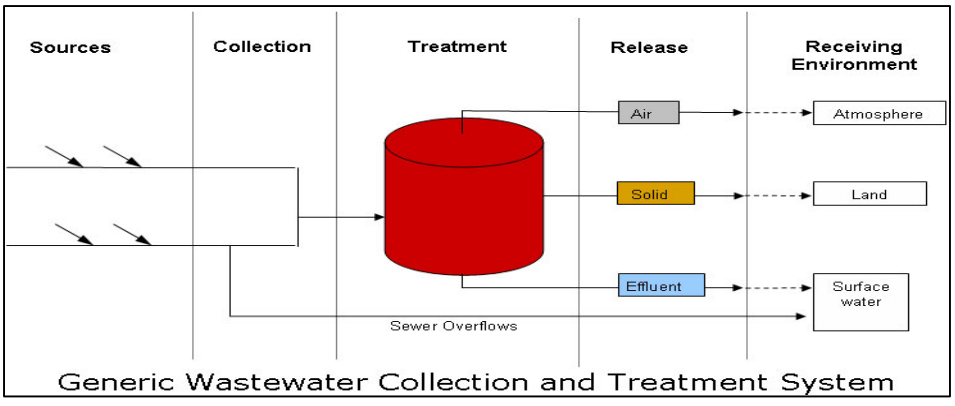
Industry is the greatest source of pollution in the United States. For instance, "about 44% of assessed stream miles, 64% of assessed lake acres, and 30% of assessed bay and estuarine square miles are not clean enough to support uses, such as fishing and swimming [17]." Some of the most common water pollutants are bacteria, mercury, phosphorus, nitrogen, and organic material that, after a process of decomposition, produce low levels of dissolved oxygen.

The implementation of water pollution prevention activities is critical to maintain the water quality and to reduce the excessive costs of treating drinking water. Therefore, knowing that water pollution may come from different sources, the need to develop pollution prevention and control measures is quite important to measure, detect, and analyze possible hazards to the environment.

According to the Ohio Environmental Protection Agency, "pollution prevention (P2) should be recognized as a core part of sustainability development and long term planning [18]." Additionally, P2 promotes the reduction or elimination of wastes before they are produced by modifying production processes, adapting new techniques, and re-using materials. Thus, the change and the implementation of these new practices will reduce the use of energy, water, and other valuable resources, and as a consequence, the reduction of wastes, achieved by changes in practices will provide a sustainable environment.

In Canada, wastewater effluents are the main source of water pollution. Wastewater may come from two sources: sanitary sewage and stormwater. The first one, sanitary sewage, mainly comes from homes, business, institutions, and industries. The second one, stormwater, "is generated from rain and melting snow that drains off rooftops, lawns, parking lots, roads and other urban surfaces [19]." Wastewater is collected by two types of sewer systems (combined sewer and separate sewer systems), and it is treated before it is released into the environment. Figure 2.10 shows a simplified process of effluent collection and treatment system of wastewater in Canada.

Figure 2.10. Wastewater Collection and Treatment System [19]



In Canada, most of the population is supplied with water coming from wastewater collection and treatment systems [19]; however, it is important to mention that wastewater passes through several cleaning processes before is provided for human use.

The Canadian Government has the responsibility for managing the collection, treatment, and release of wastewater effluent in order to ensure that standards of wastewater are accomplished. Note that standards are enforced by the Government under the "Wastewater Systems and Effluent Regulations", established in 2012 by the Government of Canada, provinces, territories, engaged municipalities, aboriginal communities, and other interested parties [19].

2.4 Heavy Metals

The presence of heavy metals in water sources close to industrial zones has received more attention in recent years than in the past due to the increasing number of environmental regulations. Metals, such as Cu, Cd, Pb, Ni, Cr, Ag, Fe, Co, Hg, and As are considered heavy metals. These metals are components of the Earth's crust that cannot be degraded or destroyed.

As trace elements some of them are essential for the human's metabolism; however, at higher concentrations they can lead to poisoning. Among these metals, this study will focus on Ni, Cu, Fe, Zn, and Pb. Table 7 shows the ranking of risk associated with various metals.

Table 2.8. Raking of risk associated with various metals [20]

Relative Priority	Environmental Risk
High	Cd
High	Pb
High	Hg
Medium	Cr
Medium	Co
Medium	Cu
Medium	Ni
Medium	Zn
Low	Al
Low	Fe

From the table we can observe that efforts should be oriented in an attempt to control the emission especially of Cd, Pb, Hg and Zn. It is important to note that, although some other heavy metals, such as Cr, Co, and Ni are classified into a lower category, this does not imply that they should not be treated and controlled. This study will analyze the presence of Ni, Zn, Pb, Fe, and Cu in water sources close to mining facilities in Newfoundland and Labrador.

2.4.1 Nickel

Nickel is the 28th element of the periodic table and it can be found silver and white in several oxidation states ranging from -1 to +4. The most common state is the +2 oxidation state in bio-systems. Physical and chemical forces, such as erosion, leaching, and precipitation, continuously redistribute nickel between water, land, and air. According Valko, Morris, and Cronin, in their article, "Metals, Toxicity and Oxidative Stress", "depending on the type of soil and pH, nickel is highly mobile [21]." For instance, at pH higher than 6.7, nickel exists as

insoluble hydroxides; however, at pH lower than 6.5, the compounds tend to be soluble. Its principal ores are the following three:

1. Pentlandite $(FeNi)_9S_8$
2. Millerite (NiS)
3. Garnierite $(NiMg)_6Si_4O_{10}(OH)_8$.

Due to its properties, nickel is mostly used in the preparation of steel and alloys and in the manufacture of batteries for corrosion resistance. According to Kelesoglu, "the metal or its compounds are also used as catalysts, dyes, fungicides, and pigments [22]." According to the Royal Science of Chemistry, "finely-divided nickel is used as a catalyst for hydrogenating vegetable oils, and nickel imparts a green colour to glass [23]." Also, nickel resists corrosion at different temperatures and that is the reason why it is used in gas turbines and rocket engines.

Nickel enters in contact with the environment in combustion processes due to the fact that nickel is present in crude oil at different concentrations. Additionally, nickel is found in surface water by natural weathering and leaching processes of minerals and rocks [22].

2.4.2 Lead

Lead is a bright and silvery metal in a dry atmosphere that, when in contact with air, begins to tarnish [24]. The contact of lead with other metals changes its properties significantly. For instance, the addition of small amounts of copper or antimony increases hardness and improves the corrosion. The addition of some other metals, such as cadmium, tin, or tellurium improves not only the hardness but also fights metal fatigue [24].

Lead is a naturally occurring metal found within the ground that occurs in small amounts in ore, such as silver, zinc, and copper; however, even though it is found in small amounts, there is an abundant supply of lead accessible for extraction. Lead has been used historically in products, such as paints, ceramics, pipes, solders, gasoline, and batteries; however, since 1980, environmental standards have helped to minimize the amount of lead in consumer products.

Due to its high density and high resistance to corrosion, lead is used for the ballast keel of sailboats. Lead is also used extensively in construction, the production of lead-acid batteries, bullets, fusible alloys, and as a radiation shield. In the Unites States more than half of the production of lead is used in the automobile industry mostly in car batteries, brake linings, and fuel hoses [25].

2.4.3 Copper

Copper is the 29th element of the periodic table and according to Valko, Morris, and Cronin, it is considered "not only a ubiquitous metal technological environment but also an essential metal for the function of most living organisms" [21]. Copper has the ability to exist in four different valence states (Cu^{0} ,$^{1+}$,$^{2+}$,$^{3+}$).

Valko, Morris, and Cronin state that "copper allows the movements of electrons through wires, but also assists catalyzing the movement of electrons within biological molecules [21]." Copper is equipped with a high redox potential that helps as a cofactor for proteins in several biological reactions, such as photosynthesis and respiration. It also serves as a cofactor for proteins in processes related to the formation of connective tissue, iron metabolism, and neurological functions [21].

Copper is commonly known to be distributed in nature as the free metal in various ores, such as cuprite, chalcopyrite, azurite, and malachite. Also, due to its ductile properties, high thermal and electrical conductivity, copper is principally used in the production of alloys, generators, transformers, and heat exchangers. It is also used as a catalyst in the chemistry industry and in the production of piping for water supply.

2.4.4 Zinc

Zinc is the 30th element of the periodic table of elements and is essential to living organisms. It is commonly found as a trace element in animals and plants. For instance, the human body contains from 1.5 to 2.5 grams of zinc mostly present in skeletal muscle and bones; however, lower concentrations of zinc can also be found in organs, such as the brain, lungs, skin kidney, and liver. Zinc can be extracted mainly from zinc blende and calamine ores.

Zinc is commonly used in the production of alloys and batteries, and as zinc oxide, to stabilise plastics. Large quantities of zinc are used in the automobile, electrical, and hardware industries. Zinc oxide is also used in products, such as paints, rubber, cosmetics, pharmaceuticals, and soaps.

2.4.5 Iron

Iron is the 26th element of the periodic table, and according to Valko, Morris, and Cronin, "is considered a major component in the production and metabolism of free radicals in biological systems [21]." Iron is commonly found in three oxidation states: Fe(II), Fe(III) and Fe(IV). It is also evidenced to be one of the most abundant elements in the Earth's crust after aluminum.

Iron is one of the 94 elements occurring naturally on Earth with a silver and grey colour. Basically, iron is found everywhere due to the fact that 5% of the Earth's crust is composed by iron. Iron rarely is found as a pure metal because of its fast reaction with oxygen to form iron oxide. The most common iron ores are magnetite, haematite, goethite, and limonite [26].

According to McNamara, in his article, "Iron is the second most abundant metal on Earth", aluminum, copper, zinc, and lead are currently the most common metals used in the industry due to their properties. For instance, iron is widely used due to its strength, abundance, and low price in the construction of machinery, automobiles, large ships, and structural components for buildings.

2.5 Impact of heavy metals on human health

The importance of sequestering metals released to the environment has increased gradually due to the unawareness of some industries of their processes. It has been proven that heavy metals released into the environment pose a hazard for human health. Heavy metal poisoning can be caused by ingestion, inhalation, and absorption through the skin or mucous membranes.

For instance, a large uptake of nickel has the following consequences on human health: (a) higher chances to develop lung, nose, larynx, and prostate cancer, (b) sickness and dizziness after exposure to gas composed of nickel, (c) respiratory failure, (d) birth defects, (e) asthma and chronic bronchitis, and (f) heart disorders.

Copper enters the human body through eating, drinking, and breathing. The absorption of copper is essential for human health; however, higher amounts of copper lead to health problems. For instance, it is commonly known that communities of people living close to smelters are more likely to develop serious health problems, such as liver and kidney damage. Communities exposed to high concentrations of copper often experience symptoms, such as irritation of the eyes, nose and mouth headaches, dizziness, vomiting, and diarrhoea.

Additionally, chronic exposure of lead has the following consequences on human health: (a) increased blood pressure, (b) decreased fertility, (c) cataracts, (d) nerve disorders, (e) muscle pain, (f) decreased hearing, and (g) memory or concentration problems. In general, the most common sources of lead exposure comes from lead-based paint in older homes, contaminated soil caused by industries, drinking water, and household dust.

In the case of zinc, acute toxicity is rare in humans, but has been reported as a result of food or beverage intake. For instance, it is has been tested that the intake of 2g of zinc sulphate can cause gastrointestinal irritation. At higher doses, symptoms include nausea, fatigue, diarrhoea, muscle pain, and fever; however, if the exposure reaches values from 100 to 300 mg/day, it may compromise the immune system [21]. It is important to note that the latter symptoms occur mostly by the intake of oral zinc supplements for medicinal purposes. Zinc is excreted in feces from 12-15 mg/day and eliminated through urine in amounts of 0.5 mg/day [21].

Iron is considered an essential element for growth and survival of most living organisms. In humans, the average-weight contains approximately 4 to 5 grams of iron. Worldwide, approximately 500 million people have problems related to iron deficiencies. In some cases

the symptoms can range from anemia to mental retardation in children [21]. On the contrary, iron excesses are less frequent in humans, but the consequences of iron overload may lead to liver and heart disease, diabetes, and immune system abnormalities [21]. In general, heavy metals can be easily absorbed by living organisms because of their high solubility in aquatic ecosystems [27]. Thus, if the metals absorbed by living organisms are beyond the maximum permitted concentrations, they can cause serious health disorders.

According to Kurniawan, Chan, Lo, and Babel, in their article, "Physico–chemical treatment techniques for wastewater laden with heavy metals", "over the past two decades, environmental regulations have become more stringent, requiring an improved quality of treated effluent [27]." Consequently, several technologies, such as chemical precipitation, coagulation–flocculation, flotation, ion exchange, membrane filtration, and adsorption have been developed and proved to be efficient; however, some technologies, such as adsorption has been demonstrated to be more efficient and cost-effective than others. The effectiveness of different technologies to treat wastewater effluent will be discussed later in this study.

2.6 Common methods used to remove heavy metal from wastewaters

The presence of heavy metals in the environment poses a risk to all living species. According to An, Park, and Kim, "Crab shell for the removal of heavy metals from aqueous solution", metals can be distinguished from other pollutants due to the fact that metals are non-biodegradable and have the ability to accumulate in living tissue [28]. Consequently, different methods, such as chemical precipitation, coagulation-flocculation, flotation, ion exchange, and membrane filtration, have being developed to remove pollutants from wastewaters.

It is important to mention that every method has its own advantages and limitations in industrial applications. Thus, the use of a specific method depends merely on the analysis of effectiveness and profitability for each technique.

2.6.1 Chemical Precipitation

Chemical precipitation has been widely used for metal removal from inorganic effluents. According to Kurniawan *et al.*, "after pH adjustment to the basic conditions (pH 11), the dissolved metal ions are converted to the insoluble solid phase via a chemical reaction with a precipitant agent, such as lime [27]."

It is important to note that the metal precipitated from the solution is in the form of hydroxide. Chemical precipitation has been proved to be an effective method for almost every metal in different concentrations at pH 11 (Table 2.9), fulfilling the requirements of the maximum authorized concentrations in effluents for countries like Thailand; however, for standards, such as US EPA, lower concentrations need to be obtained in order to accomplish the established levels of metals in effluents. Thus, in some cases, further treatment needs to be performed to comply with the US EPA standards.

Although the effectiveness of chemical precipitation has been proved to be positive, the efficiency varies depending on the metal analyzed and the concentration used in the test. Table 2.9 shows the removal efficiency for different heavy metals at different initial concentrations using chemical precipitation.

Table 2.9. Heavy metal removal using chemical precipitation [27]

Species	Precipitant	Optimum dose of precipitant (g/L)	Initial metal concentration (mg/L)	Optimum pH	Contact time (h)	Removal efficiency (%)
Zn (II)	$Ca(OH)_2$	10	450	11.0	NA	99.77
Cd (II)	$Ca(OH)_2$	10	150	11.0	NA	99.67
Mn (II)	$Ca(OH)_2$	10	1085	11.0	NA	99.30
Cd (II)	$Fe(OH)_3$	NA	37	11.0	24	96
Cu (II)	$Mg(OH)_2$	NA	16	9.5	24	80
Ni (II)	NA	NA	51.6	7.5	1	71
	NA	NA	51.6	10.5	1	85

2.6.2 Coagulation-flocculation

Coagulation-flocculation is another commonly used method to treat wastewater containing heavy metals. This method is composed of two stages. The first stage, the coagulation process, destabilizes the particle's charges by adding coagulants with opposite charges to those of the suspended solids in order to neutralize their negative charges. According to Kurniawan *et al.*, "the coagulation process destabilizes colloidal particles by adding a coagulant and results in sedimentation [27]". Non-charged solids formed through the coagulation process, called microflocs, are capable of sticking together, but are not visible without the help of a microscope.

The second stage, the flocculation process, "is intended to increase the particle size from submicroscopic microfloc to visible suspended particles [29]." Microflocs obtained from the first stage are used in a process of slow mixing. Collisions of microflocs particles during the mixing process make them bond and produce visible larger particles also called pinflocs. High molecular weight polymers, called coagulant aids, are added at this stage of the process to increase the binding of particles [29]. At the end of the flocculation process, wastewaters are

ready for the sedimentation process. It is important to note that the effectiveness of the coagulation-flocculation method depends merely on the adjustment of the pH and the addition of ferric/alum salts as the coagulant.

The following table shows the recovery of heavy metals using coagulation-flocculation and the removal efficiency of each metal in different conditions:

Table 2.10. Recovery of heavy metals using coagulation-flocculation [27]

Species	Coagulant	Dose of coagulant (mg/L)	Initial metal concentration (mg/L)	Optimum pH	Removal efficiency (%)
Zn (II)	Na_2S	100	450	11.0	99.91
Cd (II)	Na_2S	100	150	11.0	99.73
Mn (II)	Na_2S	100	1085	11.0	99.95
Cu (II)	Poly-ferric sulfate	25	20	10-11.5	99.6
Cu (II)	Poly-acrylamide	5	20	10-11.5	95

Some of the disadvantages of the coagulation-flocculation method are the high volume of sludge generated from the process and the high operational cost of performing the test due to the chemicals involved. Thus, although the coagulation-flocculation method is proven to be an effective method for removing pollutants from wastewater, the high cost to treat sludges limits its industrial applicability. It is important to mention that electrocoagulation has been used to reduce the production of sludge; however, "this technique also creates a floc of metallic hydroxides, which requires further purification [27]."

2.6.3 Flotation

Flotation, another method used to treat wastewater, is used to separate solids from a liquid phase using bubble attachment [27]. According to Verrelli, Koh, and Nguyen, "Particle–bubble interaction and attachment in flotation," "the process of flotation operates by the combination of solid particles with gas bubbles in a liquid medium, with the particle–bubble aggregates rising to the top of the liquid, where they can be removed [30]."

Table 2.11 shows the heavy metal removal efficiency using flotation for different collectors and initial concentrations.

Table 2.11 Heavy metal removal using flotation [27]

Species	Collector	Optimum dose of collector (g/L)	Precipitant	Optimum dose of precipitant (mg/L)	Initial metal concentration (mg/L)	Optimum PH	Removal efficiency (%)
Cu (II)	Chabazite	0.500	$Fe(OH)_3$	30.9	3.5	5.5	95
Ni (II)			$Fe(OH)_3$	20.0	2.0	5.5	98.6
Zn (II)			$Fe(OH)_3$	20.0	2.0	5.5	98.6
Cu (II)	Trien	0.015	SDS	NA	12.7	6.7	85
Ni (II)	Trien	0.015	SDS	NA	5.9	7.0	70
Cr (VI)	Hydrotalcite		Magnafloc	3.0	58.8	NA	95
Cu (II)	CTABr	0.020	NA	NA	474.0	8-10	99.99
Ni (II)			NA	NA	3.3	8-10	98.50
Zn (II)			NA	NA	167	8-10	99.97
Cu (II)	Zeolite	0.8	NA	NA	60	8-10	97
Zn (II)	Zeolite	0.8	NA	NA	60	8-10	97
Zn (II)	Zeolite	2	SDS	40.0	50	6.0	99
		2	HDTMA	20-40	50	9.0	96
Cu (II)		4	SDS	50.0	500	5.0	97
Cr (VI)	Surfactin-105	0.04	Ferric hydroxide	600	50	4.0	98
Zn (II)	Lycheny-sin-A	0.04	Ferric hydroxide	600	50	4.0	100
Zn (II)	SDS	0.05	NA	20.0	50	7-9	100

The effectiveness of the flotation process is based on the interaction between particles and air bubbles in three different micro-processes: the encounter or also called collision, attachment, and detachment.

According to Kurniawan *et al.*, flotation can be classified as: (i) dispersed-air flotation, (ii) dissolved-air flotation (DAF), (iii) vacuum air flotation, (iv) electro-flotation, and (v) biological flotation. Among the different flotation types, DAF is the most commonly employed in the treatment of wastewater effluent [27].

Based on the remarkable removal rates (Table 2.11), the flotation process has been considered another suitable method for treating wastewater, especially for its low material cost, for collectors, such as zeolite and chabazite that have outstanding removal efficiency. According to Kurniawan *et al.*, even though flotation has some disadvantages of being used as a wastewater treatment alone, it is considered "one of the most promising alternatives for treating metal-contaminated wastewater [27]."

2.6.4 Membrane Filtration

Membrane filtration is a well-known method not only for its capability to remove suspended solids and organic compounds, but also inorganic pollutants, such as heavy metals. Depending on the particle size to be detained, three different types of membrane filtration can be applied:

2.6.4.1 Ultrafiltration (UF)

UF utilizes a permeable membrane, with a pore size of 5 - 20 nm, to separate macromolecules and suspended solids from inorganic solutions. Under these conditions, UF only allows the passage of water and low-molecular weight solutes, collecting macromolecules with a larger pore size than the size of the permeable membrane [27].

Table 2.12. Heavy metal removal using UF [27]

Species	Kind of process	Type of membrane	Pressure (bar)	Initial metal concentration (mg/L)	Optimum PH	Rejection rates (%)
Co (II)	UF	YM1	NA	29.47	5-7	100
Ni (II)			NA	29.35	5-7	60
Cu (II)	UF	YM10	2	78.74	8.5 - 9.5	100
Zn (II)			2	81.10	8.5 - 9.5	95
Cr (III)	UF	Carbosep M2	3	20.00	6.0	95
Ni (II)	UF	UPM-20	4	10.00	NA	100
Ni (II)	UF	HL	2-5	25.00	NA	99.9
Co (II)			2-5	25.00	NA	95.0
Cd (II)	UF	$ZnAI_2O_4$-TiO_2	10	112.00	5.1	93
Cr (III)			10	52	3.6	86

Table 2.12 shows the summary of different ultrafiltration tests performed at different pressures with the use of diverse types of membranes. It is important to mention that the use of ultrafiltration to recover heavy metals ions from wastewater has been proved to be effective. For instance, depending on the membrane used in the process, "ultrafiltration can achieve more than 90% of removal efficiency with a metal concentration ranging from 10 to 112 mg/L at pH ranging from 5 to 9.5 and at 2–5 bar of pressure [27]."

According to Kurniawan *et al.*, some of the advantages of UF are a lower driving force and a smaller space requirement, as a consequence of its high packing density; however, due to membrane fouling, where the membrane's performance is degraded, UF is applied less applied today in wastewater treatment [27].

2.6.4.2 Nanofiltration (NF)

The nanofiltration method contains characteristics of reverse osmosis and ultrafiltration membranes. The significance of this method depends on the membrane due to the fact that membrane pores are smaller than in UF, and additionally the surface is charged. A charged surface rejects charged solutes, smaller than the membrane pores, along with bigger solutes, and salts presented in solution [27]. Table 2.13 shows the summary of two studies performed using nanofiltration with different types of membranes:

Table 2.13 Heavy metal removal using NF [27]

Species	Kind of process	Type of membrane	Pressure (bar)	Initial metal concentration (mg/L)	Optimum PH	Rejection rates (%)
Ni (II)	NF	HL	4	NA	4-8	96.49
Ni (II)	NF	NTR-7250	2.9	2000	3-7	94

The results from both studies, analyzing the uptake of Ni(II), show that the removal was dependent on the applied pressure and the initial metal concentrations. Also, depending on the membrane characteristics, NF can successfully remove heavy metals at different values of pH (3-8), and at a pressure of 3-4 bar [27]. Additionally, according to the results, the rejection rate for both studies was above 94%, confirming the viability of NF in the treatment of wastewater with a high metal concentration (2000 mg/L).

2.6.4.3 Reverse Osmosis (RO)

Finally, the third type of membrane filtration, reverse osmosis, is a pressure-driven membrane process where water can pass through the membrane but the heavy metals are retained. According to Kurniawan *et al.*, the importance of this method relies on the fact that "by applying a greater hydrostatic pressure than the osmotic pressure of the feeding solution, cationic compounds can be separated from water (solvent)" [27, 31]. In other words, energy is required to reverse the process of osmosis where a semi-permeable membrane allows the passage of water molecules but not the majority of salts and pollutants. The following table shows the uptake of heavy metals using reverse osmosis.

Table 2.14 Heavy metal removal using RO [27]

Species	Kind of process	Type of membrane	Pressure (bar)	Initial metal concentration (mg/L)	Optimum PH	Rejection rates (%)
Cu (II)	RO	Polyamide	7	200	4-11	98
Cd (II)			7	200	4-11	99
Cu (II)	RO	Sulfonated polysulfone	4.5	NA	3-5	98
Zn (II)			4.5	NA	3-5	99
Cu (II)	RO	ULPROM	5	50	7-9	100
Ni (II)			5	50	7-9	100
Ni (II)	RO	CPA2	15	21	7-0	97

Thus, based on the summary results of ultrafiltration, nanofiltration and reverse osmosis tests, the more effective method is reverse osmosis for removing heavy metals from inorganic solutions. The rejection rate for reverse osmosis was over 97% with a metal concentration ranging from 21 to 200 mg/L. The major disadvantage of reverse osmosis is the "high energy consumption due to high pressure required (20-100 bar) [27]"

2.6.5 Electrochemical treatment techniques

2.6.5.1 Electrodialysis (ED)

Electrodialysis is also a well-known method in the treatment of wastewater where "ionized species in the solution are passed through an ion exchange membrane by applying an electric potential [27]." The membrane used in the ED method is composed of thin sheets of plastic materials with anionic or cationic properties.

One of the main disadvantages of this technique is that concentrations higher than 1000 mg/L cannot be treated with ED. Research has proved that ED is appropriate for concentrations lower than 20 mg/L. It is important to mention that since ED is a membrane process, it requires careful maintenance in order to avoid damages to the stack [27].

2.6.5.2 Membrane Electrolysis (ME)

According to Kurniawan *et al.*, membrane electrolysis is defined as "a chemical process driven by an electrolytic potential, can also be applied to remove metallic impurities from metal finishing wastewater [27]." In comparison with electrodialysis, ME has the ability to treat wastewater with concentrations higher than 2000 mg/L or less than 10 mg/L; however, its major disadvantage is the high energy consumption.

2.6.5.3 Electrochemical precipitations

In order to enhance the removal efficiency of the traditional chemical precipitation, electrical potential has been used to maximize the recovery of metal ions from wastewater with positive

results. In general, electrochemical precipitation has been used to treat inorganic effluents with concentrations of heavy metals higher than 2000 mg/L. It is important to mention that based on the characteristics of the electrodes, the electrochemical precipitation can be used at either acidic or basic conditions.

Different studies have shown positive results for electrodialysis, membrane electrolysis, and chemical precipitations. Some of them are summarized in the following table:

Table 2.15. Electrochemical treatments for removal of heavy metals [27]

Species	Anode	Cathode	Electrical current (A/m^2)	Power consumption ($kW\ h/m^3$)	Initial metal concentration (mg/L)	Optimum PH	Removal recovery efficiency (%)
Ni (II)	Platinum	Stainless steel	400.0	NA	11.72	NA	69
	oxide-based						
	coated Ti						
Co (II)			25.0	NA	0.84	NA	90
Cd (II)	Nation 450	Selemion	150.0	NA	2000	NA	13
Ni (II)	Activated Ti	Metal granule	325.0	4.2×10^3	2000	5.5	90
Cr (VI)	Carbon aerogel	Carbon aerogel	0.8	NA	8	2.0	98.5
	Iron rotary	Iron rotary	113.0	7.9×10^3	130	8.5	99.6
	Fe_2-O_3	NA	1.7	12	NA	10-11	77 - 100
	Fe_2-O_3	NA	6.7	20	2100	10-11	85.1
Ni (II)	Ti(II)	Stainless sheet	600.0	3.43×10^3	40000	NA	80 - 85

Although the removal efficiency of heavy metal ions is proven to be positive using electrochemical treatment technologies, other methods, such as nanofiltration, ultrafiltration, and reverse osmosis, for treating wastewater, have shown to be more effective in the recovery of heavy metals ions. For instance, based on the summary results, ED is not an efficient method treating organic effluents with concentrations higher than 1000 mg/L. Methods, such as NF, have proven to be effective for heavy metal ions in concentrations of 2000 mg/L.

2.6.6 Ion exchange

Ion exchange is considered one of the most common methods used to recover non-ferrous and precious metals from inorganic effluents. In this method, a reversible interchange of ions between the solid and liquid phases occurs, where "an insoluble substance (resin) removes ions from an electrolytic solution and releases other ions of like charge in a chemically equivalent amount without any structural change of the resin [27]."

Ion exchange is proven to be effective in the recovery of non-ferrous and precious metals from inorganic effluents in concentrations ranging from 10 to 100 mg/L. Based on the characteristics of the ion exchanger, heavy metals can be recovered in acidic conditions with pH values from 2 to 6 [27].

One of the major advantages of this method, compared with chemical precipitation, is that ion exchange does not provide any sludge disposal problems, and as a consequence, is widely used in wastewater treatment. Another advantage of ion exchange is that this method is convenient for fieldwork due to the portability of the required equipment, making ion exchange easy and reliable to perform.

2.6.7. Adsorption

During the years, adsorption has become one of the major techniques used to recover metal ions from wastewater due to its main properties of transferring a substance from the liquid phase to the surface of a solid by chemical and/or physical interactions.

2.6.7.1 Bio-sorption

According to An, Park, and Kim, "the phenomenon that metallic ions are concentrated by even dead cells through purely physico-chemical process is called bio-sorption". [28] The importance of this method is that, once the metals are sorbed on the surface of the adsorbent and desorbed by proper treatment, the biomass can be repeatedly reused.

Bohumil Volesky, one of the major researchers in the field, defines bio-sorption as "the property of certain biomolecules (or types of biomass) to bind and concentrate selected ions or other molecules from aqueous solutions [3]."

It is important to note that pollutants can be removed from aqueous solutions by living microorganisms and also by dead biological material; however, due to the fact that living microorganisms require nutrient supplies and bioreactor systems, the use of non-living biomass has advantages over living microorganisms removing pollutants from aqueous solutions [3].

The use of bio-sorbents to recover pollutants from wastewater is a relatively new technology that has advantages not only in recovering pollutants, reducing the risk of biological sludges, and maintaining high efficiency, but it also can be performed at a low cost.

According to D Park, and J Park, the main factor to be taken into account, when choosing biomass for industrial purposes is its availability and cheapness [3]. Thus, biomass can come from:

1. Industrial wastes

2. Organisms easily obtained and in large amounts in nature
3. Organisms that can be grown fast.

Table 2.16 shows the most common types of biomass used in the preparation of bio-sorbents.

Table 2.16. Types of biomass that have been used for preparing bio-sorbents [3]

Category	Examples
Bacteria	Gram-positive bacteria (*Bacillus* sp., *Corynebacterium* sp., etc.), gram-negative bacteria (*Escherichia* sp., *Pseudomonas* sp., etc), *cyanobacteria* (*Anabaena* sp., *Synechocustis* sp., etc.)
Fungi	Molds (*Aspergillus* sp., *Rhizopus* sp., etc), mush-rooms (*Agaricus* sp., *Trichaptum* sp., etc.), and yeast (*Saccharompyces* sp., *Candida* sp., etc.)
Algae	Micro-algae (*Clorella* sp., *Chlampydomonas* sp., etc.), macro-algae (green seaweed (*Enteromorpha* sp., *Codium sp* ., etc.) brown seaweed (*Sargassum* sp., *Ecklonia* sp., etc.), and red seaweed (*Geildium* sp., *Porpphyra* sp., etc.)).
Industrial wastes	Fermentation wastes, food/beverage wastes, activated sludges, anaerobic sludges, etc.
Agricultural wastes	Fruit/vegetable wastes, rice straws, wheat bran, soybean hulls, etc.
Natural residues	Plant residues, sawdust, tree barks, weeds, etc.
Others	Chitosan-driven materials, cellulose-driven materials, etc.

Depending on the biomass selected, a chemical/functional group can attract different pollutants. These groups can consist of amide, amine, carbonyl, carboxyl, hydroxyl, imine, imidazole, sulfonate, sulfhydryl, thioether, phenolic, phosphate, and phosphodiester groups [3].

The group analyzed in this study is the group amino presented in the bio-sorbent; however, the presence of the functional group on the Lobster's shell does not guarantee the removal of heavy metals from water sources at low temperatures.

The importance of any given chemical/functional group for the adsorption of a certain solute depends on several factors, such as the number of reactive sites in the bio-sorbent, the accessibility of the sites on the surface of the adsorbent, the chemical state of the sites, and the affinity between the adsorbent and the sorbate in solution [3].

It is important to clarify that the adsorption of different pollutants with the use of bio-sorbents not only depends on the chemical/functional group, but also on different physical and chemical factors that can affect the overall bio-sorption of pollutants in aqueous solutions.

For instance, in adsorption systems of ionic metals, factors, such as pH, temperature, ionic strength, initial pollutant concentration, bio-sorbent dosage, bio-sorbent size, agitation speed, and the coexistence of other pollutants, notably impact the uptake of solutes in the system [3]. Among these factors, the pH is extensively proven to be the most important factor affecting the uptake of an adsorption system.

According to D Park, and J Park the pH affects the chemistry of the pollutants, the chemical/functional group of the adsorbent, and the competition with coexisting pollutants in a solution [3]. It is also known that increments in the solution pH benefit the uptake of cationic metals; however, the uptake is reduced for anionic metals when increments in the solution pH occur. Table 2.17 shows the main factors affecting on bio-sorptive removal of adsorptive pollutants, such metals or dyes.

Table 2.17. Effects of batch processing factors on bio-sorptive removal of adsorptive pollutants, such as metals and dyes [3]

Process factors	Effects on biosorption of pollutants
Solution pH ↑	It enhances biosorptive removal of cationic metals or basic dyes, but reduces that of anionic mtals or acidic dyes.
Temperature ↑	It usually enhances biosorptive removal of adsorptive pollutant by increasing surface activity and kinetic energy of the adsorbate, but may damage physical structure of biosorbent.
Ionic strenght ↑	It reduces biosorptive removal of adsorptive pollutant by competing with the adsorbate for binding sites of biosorbent.
Initial pollutant conc. ↑	It increases the quantity of biosorbed pollutant per unit weight of biosorbent, but decreases its removal efficiency.
Biosorbent dosage↑	It decreases the guantitiy of biosorbed pollutantper unit weight of biosorbent, but increases its removal efficiency.
Biosorbent size ↓	It is favorable for batch process due to higher surface area of the biosorbent, but not for column process due to its low mechanical strength and clogging of the column.
Agitation speed ↑	It enhances biosorptive removal rate of adsorptive pollutant by minimizing its mass transfer resistance, but may damage physical structure of biosorbent.
Other pollutant conc. ↑	If coexisting pollutant competes with a target pollutant for binding sites or forms any complex with it, higher concentration of other pollutant(s) will reduce biosorptive removal of the target pollutant.

Studies have proven that higher values of pH enhance the bio-sorption of metals in aqueous solutions at temperatures ranging from 20 to 35 °C; however, the recovery of heavy metals at low temperatures has not been tested. Thus, the purpose of this study is to analyze the recovery of heavy metals by using biomass-marine wastes in synthetic water in order to examine the uptake capacity of the bio-sorbent at 0 °C. It is important to mention that experiments will be performed at 0 °C. with the purpose of analyzing the essential characteristics needed to remove

heavy metals from wastewater in discharge points, close to mining industries in Newfoundland and Labrador, where temperature reaches values below 0 °C.

Research has been done that tries to enhance the efficiency of each bio-sorbent to recover pollutants from water sources with positive results. Some physical and chemical modifications have been tested and proven to be effective for different bio-sorbents. Some of these modifications can be seen in the following table:

Figure 2.18. Modification methods for converting raw biomass into better bio-sorbents [3]

Category		Detailed methods
Physical modification		Autoclaving, steam, thermal drying, lyophilization,cutting, grinding, etc.
Chemical modification	Pretreatment (washing)	Acids (HCl1, H2SO4, HNO3, H3PO4, citric acid, etc.), Alkalis (NaOH, KOH, NH4OH1, Ca(OH)2, etc.), Organic solvents (methanol, ethanol, acetone, toluene, formaldehyde, epichlorohydrin, salicylic acid, NTA, EDTA, SDS, L-cysteine, Triton X-100, etc.), and Other chemicals (NaCl, CaCl2, ZnCl2, Na2CO3, NaHCO3, K2CO3, (NH4)2SO4, H2O2, NH4CH3COO,etc.).
	Enhancement of binding groups	Amination of hydroxyl group, carboxylation of hudroxyl group, phosphorylation of hydroxyl group, carboxylation of amine group, amination of carboxyl group, saponification of ester group, sulfonation, xanthanation,thiolation, halogenation, oxidation, etc.
	Elimination of inhibiting groups	Decarboxylation/elimination of carboxyl group, deamination/elimination of amine group, etc.
	Graft polymerization	High energy radiation grafting (using y-irradiaton, mocrowave radiation, electro-magnetic radiation, etc.); Photochemical grafting (with/without sensitizers like benzoin ethyl ether, acrylated azo dye and aromatic ketones under UV light); and Chemical initiation grafting (using ceric ion, permanganate ion, ferrous ammonium nitrate/H_2O_2, $KMnO_4$/citric acid, etc.)
Cell modification (during growth)	Culture optimization	Optimization of culture conditions for enhancing biosorptive capacity of cells
	Genetic engineering	Over-expression of cysteine-rich peptides (glutathione, phytochelatins, metallothioneins, etc.); and Expression of hybrid proteins on the surface of cells.

Excellent bio-sorbents can be produced by modifying the structure of each biomass; however, the enhanced bio-sorbents increase in price, and as a result, the application of bio-sorption is no longer profitable for industrial purposes. Additionally, some classes of biomass need to be immobilized due to their physical characteristics; therefore, the cost of modifying raw biomass and the cost of immobilization need to be taken into account for industrial applications. It is important to mention that one of the main benefits of bio-sorption is their low cost compared to commercial adsorbents, such as ion-exchange, resins, or activated carbons.

Chapter 3

3. Properties, characterization, and application areas of chitin and its derivatives

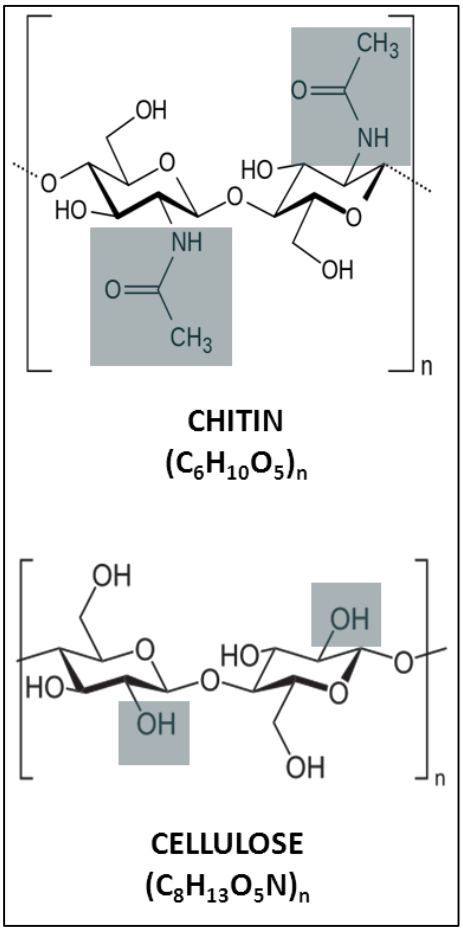
3.1 Origin of Chitin

The etymology of the word *chitin* comes from the French word *chitine* and the Greek word *khitôn,* which means tunic. In nature, chitin is the most common biopolymer found after the cellulose molecule. Chitin is mainly found in crustaceans, insects and microorganisms; however, the main source of chitin is the shell of crustaceans, such as shrimps, crabs, and lobsters. Due to the biological properties of chitin, such as bio-degradability, bio-compatibility, non-toxicity, and antimicrobial activity, chitin and its derivatives have become a considerable source for a wide range of friendly environmental and health applications. Applications of chitin and its derivatives will be described in this chapter.

3.2 Chemical and structural properties of Chitin and its derivatives

Chitin is a polysaccharide made of repetitive units of carbohydrate linked by glycosidic bonds. According to P. Dutta, J. Dutta, and Tripathi, "chitin is considered as cellulose derivative, even though is does not occur in organisms producing cellulose [33]." Cellulose is a polymer composed of D-glucose units linked in β-(1-4), while chitin is composed of 2-acetamido-2-deoxy- β -D-glucose units linked in β-(1-4). In other words, chitin is structurally identical to cellulose, but it has acetamide groups ($-NHCOCH_3$) at the C-2 positions. The functional group that makes chitin different from cellulose is highlighted in blue in Figure 3.1 [34, 35].

Figure 3.1. Chemical structure of chitin and cellulose [36]

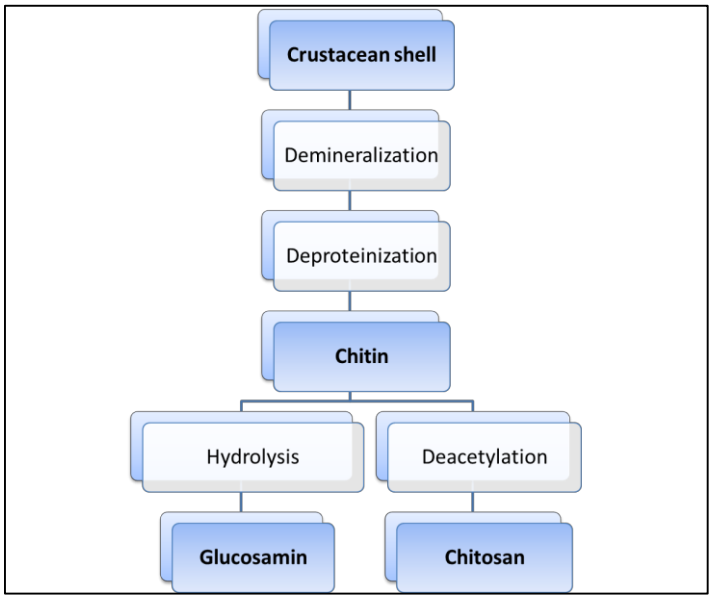


In nature, chitin exists in 3 forms, α, β, and γ. The first one, α –chitin, is the most abundant form that can be isolated from crustaceans while the second one, β-chitin, is mainly isolated from squids, and the third one, γ-chitin, is isolated from fungi and yeast [37]. The structural conformation of α -chitin causes the formation of strong hydrogen bonds rendering the molecule extremely rigid and insoluble in water and in organic solvents [35].

Because of the low solubility of chitin, extensive literature can be found on the study of chitin's derivatives, such as chitosan, glucosamines, and oligosaccharides, which contain weaker hydrogen bonds that increase their solubility in water and in organic solvents (Figure 3.2).

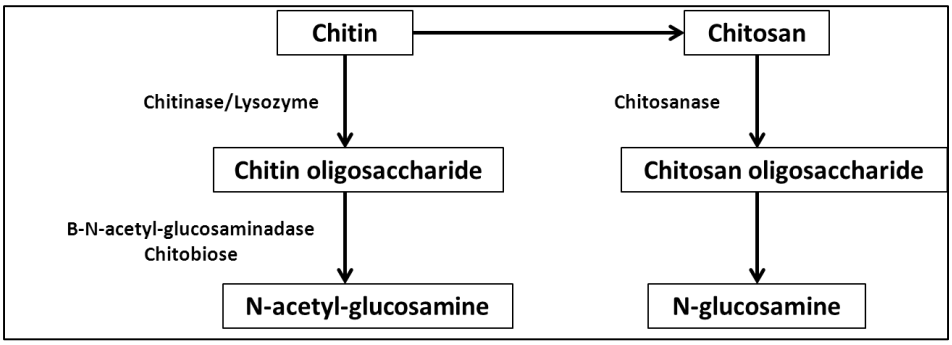
In the industry, chitin is isolated from the shell of crustaceans by mechanical systems that wash and crush the shells. The shells are then demineralized with hydrochloric acid and deproteinized with an alkaline solutions (Figure 3.12).

Figure 3.2 Isolation of chitin from crustacean shells [38]



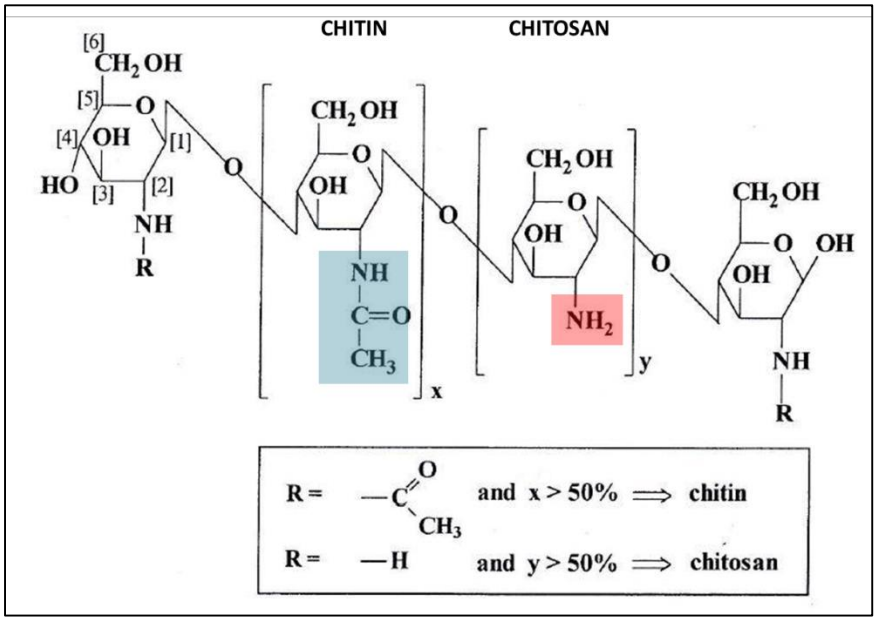
In chemistry, chitosan is obtained by the deacetylation of chitin with an alkaline solution, such as sodium hydroxide. In nature, some fungal strains are known to produce chitosan instead of chitin and use chitosan as a structural polymer for the formation of their cell wall. Chitosan also participate in the formation of the cuticle of insects [39]. These natural chitosan molecules are synthesized by a variety of chitin synthetases and chitin deacetylases [40] (Figure 3.3).

Figure 3.3. Chitin and its derivatives [40]



The distinction of chitin and chitosan depends on their degree of acetylation. When the number of acetamido group (C_2H_4NO) from the chitin is higher than 50%, the biopolymer is called chitin, whereas when the number of amino group from the chitin is higher than 50%, the biopolymer is called chitosan (Figure 3.4).

Figure 3.4. Chemical structure of chitin and chitosan [40]



Oligosaccharides and glucosamines from chitin and chitosan can be obtained by the hydrolysis of chitin from crustaceans or can be obtained by the hydrolysis of specific enzymes. These oligomers have the particularity of being soluble in water and in organic solvents.

3.3 Applications of chitin and his derivatives

Due to the chemical properties of chitin and its derivatives, the Environmental Protection Agency (EPA) of the United States has considered these biopolymers as non-toxic for humans or animals with no ecological risks. Thus, due to the massive availability of chitin on crustaceans and its bio-properties, chitin and its derivatives are widely studied in different areas, such as, health, drug, textile, and food industries.

3.3.1 Application in Cosmetics

The Meron Group, an ISO 9001:2000 certified company involved in the development of marine biopolymers, such as chitin and chitosan, have developed several chitin and chitosan-based skin-care and hair-care products. These products have been developed as a consequence of the antimicrobial and bio-compatibility properties of chitin and chitosan. Chitin is also known in cosmetics as an effective hydrating agent that supplies water and avoids dehydration. According to Rinaudo, in her article, "Chitin and Chitosan: properties and applications", chitin is widely used in cosmetic products, such as, skin moisturizers, acne treatments, and hair and oral care products [41].

3.3.2 Application in food industry

Due to their antimicrobial properties, chitin and its derivatives have been employed in agriculture to enhance the antimicrobial defenses of plants [42]. Several studies have shown that conventional food additives can be replaced by chitin and its derivatives to enhance the preservation of food and to avoid bacterial contamination [43-46]. According to Rinaudo,

chitosan is also used in the stimulation of plant growth, frost protection, and as fertilizer that improves overall crop yield [41].

3.3.3 Application in drug delivery

To improve the efficacy and the safety of drug delivery, researchers are looking and conducting studies on the designing of novel systems for drug delivery. Their studies focus on the use of degradable and bio-compatible polymers that can resist the acidic environment in the human body. Consequently, drugs will be delivered into the target site within the human body, and the biopolymer will be degraded into non harmful components for the organism.

For the improvement of drug delivery systems, chitosan has been used as a drug carrier to deliver drugs at specific sites. For this purpose, Kwon *et al.*, have developed a method that allows chitosan molecules to be bound to a biodegradable linker attached to a drug. After delivery, the linker bond to chitosan is cleaved by hydrolysis or by specific enzymes at the site of the delivery to release the drug [47].

3.3.4 Application in textile and paper industries

Due to the non-toxicity and bio-degradability of chitin and its derivatives, chitin and chitosan have been extensively employed in the paper industry as an alternative to remove toxic chemicals from wastewater used in production processes. The use of chitin and chitosan in the treatment of wastewater reduce the negative impact of toxic chemicals on the

environment. Also, chitin and its derivatives have also been employed during the production process for improving the quality of paper [48].

3.3.5 Application in the regeneration of tissue

Due to the structural properties, the bio-compatibility, and the antimicrobial properties of chitin and its derivatives, numerous studies have analyzed the use of biopolymers in biomedical application for the regeneration of tissues. According to Jayakumar, Prabaharan, Kumar, Nair, and Tamara, in their article, "Biomaterials based on chitin and chitosan in wound dressing applications", "wound dressing is one of the most promising medical applications for chitin and chitosan. The adhesive nature of chitin and chitosan together with their antifungal and bactericidal character, and their permeability to oxygen, is a very important property associated with the treatment of wounds and burns [49]." Several types of chitin-based wound dressings have been commercialized due to their properties, which include the ability to stimulate cell proliferation and to prevent infection. Oligosaccharides that derivate from chitin and chitosan have been used for wound dressing applications to accelerate wound healing. Components of living tissue, such as glycosaminoglycans, have been reported to have structural similarities with oligosaccharides that derivate from chitin and chitosan [50].

Furthermore, chitosan wound dressing for controlling bleeding and microbial infection have been designed with outstanding results [51, 52]. Wound healing is a complex process that requires the response of several cell types in order to achieve the restoration of skin architecture and function. Chitin and its derivatives have proved to be effective dressing materials for wound healing [49].

3.3.6 Application in wastewater treatment for the removal of heavy metals

Water management is essential to provide clean water supplies and to protect the environment and human health from toxic substances released into water sources. According to D.Zhou, Zhang, J Zhou, and Guo, in their article, "Cellulose/chitin beads for adsorption of heavy metals in aqueous solution" since environmental protection has become an important issue, especially during the last few decades, biosorption has become a successful technique for the removal of metals in aqueous solutions, and as a consequence, pollutants can be removed by inexpensive biological materials, such as bacteria, yeast, fungi, algae, chitin and chitosan [53].

Indeed, several batch experiment studies have shown that chitin and chitosan have the capacity to act as bio-absorbents for the removing of toxic metals from waste water. Some studies have shown that chitin and chitosan have the capacity to absorb toxic heavy metals, such as cadmium, copper, mercury, zinc, lead, and nickel [54]

It is important to mention that in most cases the adsorption capacity of chitosan is higher than chitin for most heavy metals. Figure 3.5 shows the adsorption capacity of chitin and chitosan for different metals.

Table 3.1: Absorption capacity of chitin and chitosan for toxic heavy metals from several batch experiments studies

Adsorbate	Adsorbant	Absorption capacity	Reference
Hg	Chitosan	815 mg/g	[54]
Cu	Chitosan	222 mg/g	[56]
Ni	Chitosan	164 mg/g	[57]
Zn	Chitosan	75 mg/g	[57]
Pb	Chitosan	72 mg/g	[58]
Cd	Chitin	14.0 mg/g	[59]
Cu	Chitin	5.9 µmol/g	[60]
Cd	Chitosan	5.93 mg/g	[61]

Chapter 4

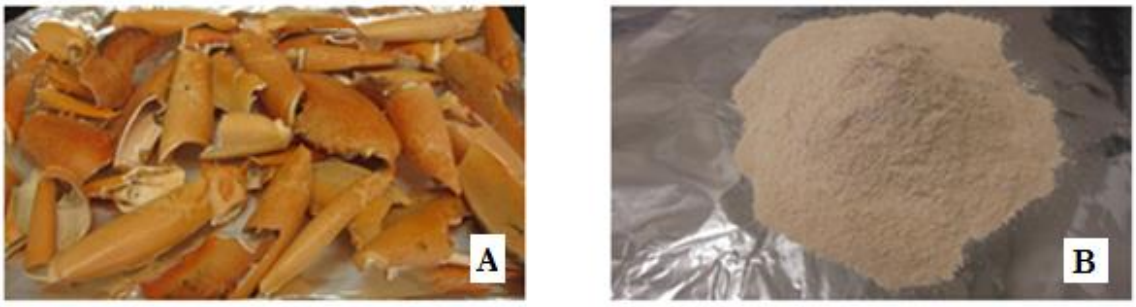
4. Materials and Method

4.1 Materials

4.1.1 Preparation of the adsorbent

Lobster shells have been collected from fish markets in St John's, Newfoundland and Labrador, Canada. The adsorbent was boiled, washed, and dried at 70 °C for 24 hours. The adsorbent was then milled and sieved by 0.25 mm mesh and stored at 4 °C (Figure 4.1).

Figure 4.1. (**A). Lobster shells collected from local fish markets in Newfoundland and Labrador. (B). Lobster shell powder (bio-sorbent)**



4.1.2 Preparation of the liquid phase

In order to perform different tests, adsorbate stock aqueous solutions of Cu, Zn, Fe, Pb, and Ni at 100 ppm were prepared in concentrations of pH from 1 to 7. Adsorbate stock solutions were diluted from 100 ppm to 20 ppm with distilled water at different values of pH (1, 3, 5, and 7). All stock pH solutions were prepared with sulphuric acid diluted with water. It is

important to mention that analytical grade reagents were used in all cases for the preparation of solutions.

4.2 Methods

4.2.1 Batch absorption assay

According to Seidel-Morgenstern, "static methods of measuring adsorption isotherms [such as Batch tests] do not analyse concentration time curves and use only the information of equilibrium states [62]." Consequently, in order to determine the adsorption of the non-ferrous metals by chitin from lobster biomass, batch absorption assays were performed by adding 1 mg/mL of lobster shells with a mixture of non-ferrous metal at different concentrations and different values of pH. Each solution was shacked at 115 rpm for 25 hours in closed vessels. All reactions were performed at room temperature (25 °C) and at zero degrees Celsius (0 °C). A 3 mL aliquot of solution was taken at different times of the incubation in order to measure the effect of time on the uptake of heavy metals. Each aliquot was filtered with Whatman filter paper (70mm) and measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES). ICP is commonly used to determine metal concentration in the aqueous phase.

The effect of pH on adsorption was analyzed by using different values of pH, ranging from 1 to 7. The effect of initial concentration on the rate of adsorption was also examined by using concentrations from 20 to 100 ppm. Finally, the effect of temperature was also investigated by testing the uptake capacity of the lobster biomass at 0 °C and at room temperature. It is important to mention that one of the main purposes of this study is to analyse the possibility of recovering heavy metals from wastewater effluent at low temperatures in Newfoundland

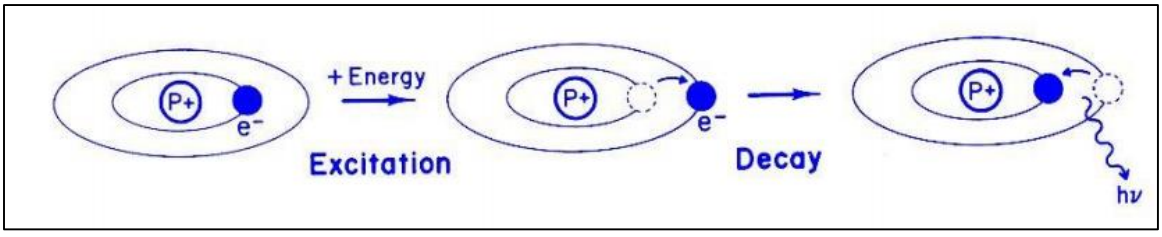
and Labrador. It is also important to mention that all adsorption assays were performed two times, and the resultant average values were used for the analysis.

4.2.2 Inductively Couple Plasma Mass Spectrometry (ICP-AES)

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), also called inductively coupled plasma optical emission spectrometry (ICP-OES), is a technique employed for the detection of trace metals. This technique is based on the use of inductively coupled plasma to produce excited atoms at wavelengths distinctive of a particular element. The strength of a wavelength is used to identify the concentration of a particular metal.

According to Gong, the electrons of an atom absorb the energy required to jump to higher energy levels, and as a consequence, when they return to normal states, they emit typical photons of energy that can be used to determine the types and the concentrations of the elements present [63]. The following figure shows an example of the inductively coupled plasma atomic emission spectrophotometry's mechanism.

Figure 4.2. Inductively coupled plasma atomic emission spectrophotometry's mechanism [63]



It is important to mention that due to its high specificity, capability, and outstanding detection limits, this technique is widely used in a variety of applications, such as the analysis of leaching

from mine sites, geochemical prospecting, and in sediment examination According to Gong some of the benefits of using ICP-AES include: "(1) Detection Limits down to parts per trillion for some elements; (2) rapid simultaneous determination of selected elements; (3) selective determination of other elements in sequential mode; (4) good linear range – up to hundreds of parts per million for alkalis; (5) can detect most cations and anions examined in one sample; and (6) suitable for routine analyses of multiple samples [63]."

4.2.3 Isotherm adsorption analysis

The adsorption process involves a solid phase (adsorbent) and a liquid phase (solvent, normally water) containing the dissolved species to be adsorbed (adsorbate) [3]. The measurement of interactions between the adsorbate and the absorbent (liquid and solid phase) is fundamental in the evaluation of the viability of the bio-sorbent used to recover heavy metal from wastewater effluent. Thus, mechanistic or empirical methods can be used for measuring adsorbate-adsorbent interactions. On one hand, mechanistic methods explain, represent, and predict experimental behaviour. On the other hand, empirical methods, reflects experimental curves. Empirical methods have been used considerably with good rates of success. Most of the empirical methods involve two to four parameters to fit batch equilibrium isotherm curves to different bio-sorbents.

Among all the empirical models, Langmuir and Freundlich models are the most used in adsorption isotherm analysis with positive results for single solute systems; however, for multicomponent systems, their assumptions are excessively ideal for fitting experimental data. Table 4.1 shows equilibrium isotherms models used for single component systems [3].

Table 4.1. Equilibrium isotherm models for single component systems [3]

System	Expression	Equation form
Single component	Langmuir	$q = \frac{q_m b C_e}{1+bC_e}$
	Freundlich	$q = KC_e^{1/n}$
	Temkin	$q = \frac{RT}{b}\ln(aC_e)$
	Dubinnin-Radushkevich	$q = q_D \exp[-B_D\{RT\ln(1+1/C_e)\}^2]$
	Langmuir Freundlich	$q = \frac{q_m b C_e^{1/n}}{1+bC_e^{1/n}}$
	Redlich - Peterson [93]	$q = \frac{aC_e}{1+bC_e^{n}}$

Single component isotherm models are used for systems composed by only one adsorbate. Some other methods, such as Langmuir-Freundlich and Redlich-Peterson are extensions of the initial Langmuir model with some other assumptions. It important to mention that although Langmuir and Freundlich models for single component systems are ideal due to their assumptions, the use of them provide a general indication of the adsorption behaviour of an absorbent.

This study will focus on the use of single and multi-component models due to the composition of the liquid phase. It is important to mention that the experimental data needs to describe the adsorption behaviour of the single component system in order to be employed in a multicomponent system. Thus, the initial analysis of this study will be focused on the evaluation of the experimental data using Langmuir and Freundlich for single component

systems. Based on the results of the single adsorption systems, Langmuir and Langmuir-Freundlich multicomponent models will be used in order to fit the experimental data and conclude about the efficiency of the solid phase (adsorbent). Table 4.2 presents some of the models used for analyzing multi-component isotherm systems.

Table 4.2. Equilibrium isotherm models for multi component systems [3]

System	Expression	Equation form
Multicomponent	Langmuir	$q_i = \frac{q_{mi} b_i C_i}{1 + \sum_{i=1}^{N} (b_i C_i)}$
	Langmuir Freundlich	$q_i = \frac{q_{mi} b_i C_i^{1/ni}}{1 + \sum_{i=1}^{N} (b_i C_i^{1/ni})}$
	Redlich - Peterson	$q_i = \frac{a_i C_i}{1 + \sum_{i-1}^{N} (b_i C_i^{ni})}$
	Freundlich	$q_i = K_i C_i \left(\sum_{j=1}^{k} a_{ij} C_j \right)^{n_i - 1}$

According to Gerente, Lee, Le Cloirec and McKay, "the importance of obtaining the best-fit isotherm becomes more and more significant, because as more applications are developed, more accurate and detailed isotherm descriptions are required for the design of treatment systems [64]"; however; according to Carvalho, Abreu, Benachour, Sales, Barauna and Sobrinho, in their article, "Applying Combined Langmuir–Freundlich Model to the Multi-Component Adsorption of BTEX and Phenol on Smectite Clay," due to the complexity of

some adsorption systems, there is no model that can be universally applied to every model [65].

4.2.3.1 Individual Analysis

4.2.3.1.1 Langmuir Isotherm

The Langmuir isotherm refers to the adsorption of molecules on a solid surface at a fixed temperature. The Langmuir isotherm model is the most common method used to measure the amount of adsorbate sorbed on an absorbent as a function of concentration or partial pressure. The Langmuir's equation, for a single component system, can be expressed as follows:

$$q_e = \frac{q_m\, bC_e}{1 + bC_e}$$

Where, q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g); Ce is the equilibrium concentration of the sorbate in the solution (mg/L); q_m is the maximum adsorption capacity of the solute (mg/g); and "b is the constant related to the free energy of adsorption (L/mg) [66]."

Irving Langmuir, in his model for the adsorption of species onto simple surfaces, made the following assumptions:

1. The surface of the absorbent is totally homogeneous with no corrugations
2. All the adsorbing sites have the same energy
3. Adsorption is reversible

4. Each adsorbing site can hold no more than one molecule at a time. This is also known as single-layer adsorption
5. Adsorbate molecules have no interactions on adjacent sites between them

The linearization of the Langmuir isotherm equation is necessary to determine the constants q_m and b by plotting $\frac{1}{C_e}$ vs. $\frac{1}{q_e}$. Langmuir's equation can also be expressed in a linear form as follows:

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{bq_m}\right)\left(\frac{1}{C_e}\right)$$

It is important to mention that q_e can be calculated with the use of the experimental data. The amount of adsorption (q_e) can be calculated by using the following equation:

$$q_e \left[\frac{mg}{g}\right] = \frac{V * (C_i - C_f)}{S},$$

q_e is defined as "the amount of metal ions adsorbed onto the unit amount of the sorbents [53]." V is the volume of the liquid phase that contains the sorbate and the sorbent. Volume is measured in liters (L). C_i and C_f are the initial and the final concentrations of the metals in the solution, respectively. Concentrations are measured in milligrams per liter (mg/L). S is the amount of the added bio-sorbent on the dry basis. The bio-sorbent is measured in grams (mg).

Based on the uptake capacity (q_e) of the bio-sorbent to recover each sorbate we can plot the different isotherms for the individual analysis. It is also important to mention that "although the Langmuir assumptions seem too ideal for actual adsorption systems, the isotherm has been

found useful in data interpretation [67]." According to Lee, "when one decides to use the Langmuir isotherm to interpret the data, one should be aware that this isotherm does not provide adequate fit for many single-solute systems [67]."

4.2.3.1.2 Freundlich Isotherm

The Freundlich isotherm, also known as the van Bemmelen isotherm, assumes heterogeneous surface energies distributed exponentially. It is important to mention that, although the Freundlich isotherm is an empirical model, this model fits experimental data over a large range of concentrations. The Freundlich isotherm model is expressed as

$$q_e = \mathrm{K}\, C^{1/n}$$

where q_e is the amount adsorbed per gram of the adsorbent, K is one of the Freundlich parameters related with the total adsorption capacity, and 1/n is the other Freundlich parameter related with the adsorption intensity.

In order to find the Freundlich parameters, the isotherm model can be linearized as follows:

$$\mathrm{Log}\ q_e = \mathrm{Log\ K} + 1/\mathrm{n}\ \mathrm{Log}\ C_e$$

A plot of (Log q_e) versus (Log C_e) yields a slope = 1/n and an intercept =K. Depending on the slope, the adsorption energy varies. A higher slope represents lower adsorption energy and a lower slope represents good affinity (higher adsorption energy) between the liquid and solid phase.

4.2.3.2 Multicomponent Analysis

4.2.3.2.1 Langmuir (multicomponent)

The Multicomponent isotherm, developed by Butler and Ockrent, assumes the use of different adsorbates in one adsorption system. The Langmuir equation, for a multi component system, can be expressed as follows:

$$q_i = \frac{q_{mi}\ b_i C_i}{1 + \sum_{i=1}^{N}(b_i C_i)}$$

Where, q_i is the amount of solute "i" adsorbed per unit weight of the adsorbent at equilibrium (mg/g); Ci is the equilibrium concentration of the sorbate "i" in the solution (mg/L); q_{mi} is the maximum amount of solute "i" adsorbed per unit weight of the adsorbent (mg/g) and "b is the constant related to the free energy of adsorption for the solute "i" (L/mg) [66].

According to D. Park, Yun, and J Park, single component systems have been positively extended to multicomponent models. Among the single-component models transformed, the Langmuir model has proven to fit experimental data reasonably well [3].

It is important to note that the multicomponent Langmuir isotherm can only be applied when each solute predicts the adsorption behaviour in a single component system. Some of the assumptions of the multicomponent Langmuir isotherm are:

1. The surface of the absorbent is totally homogeneous with no corrugations
2. All the adsorbing sites have the same energy

3. Adsorption is reversible
4. Each adsorbing site can hold no more than one molecule at a time. This is also known as single-layer adsorption
5. Adsorbate molecules have no interactions on adjacent sites between them

According to Lee, one of the major disadvantages of this method is that it violates Gibbs' adsorption equation and is thermodynamically inconsistent; however, this method is probably one of the most used in the comparison of different models.

4.2.3.2.2 Freundlich Isotherm (multicomponent)

The multicomponent Freundlich isotherm, derived by Sheindorf, Rebhun, and Sheintuch in 1981, assumes that for each component, there is an exponential distribution of energy which is similar to the distribution in the single component system [68]. It is important to note that each sorbate analysed needs to obey the Freundlich mono-component isotherm in order to be employed in a multicomponent systems. The Freundlich equation, for a multi component system, can be expressed as follows:

$$q_i = K_i C_i \left(\sum_{j=1}^{k} a_{ij} C_j \right)^{n_i - 1}$$

Where a_{ij} is the competition coefficient between the adsorbate "i" and "j". The calculation of each competition coefficients is based on the experimental data obtained in a bi-component system. In the case that more than two solutes are presented in the system, the calculated values for a bi-component system can be used to predict the adsorption behaviour of a

complex (more than two solutes) system. The values for a_{ij} goes from zero (no competition is present) to values normally lower than ten (a high degree of competition is present between the solutes).

One of the major disadvantages about the multicomponent Freundlich isotherm is that the model also violates Gibbs' adsorption equation. Nevertheless, due to the versatility of this model to fit several single component systems, it is also often employed in its multicomponent form.

4.2.3 Kinetics adsorption analysis

Batch kinetics modeling is usually employed to analyze the response of the adsorption system due to changes produced by variations in the experimental conditions. The model results can be impacted by the "adsorbent size, initial concentration, maximum uptake capacity of adsorbent, mass transfer coefficients, and solute diffusivity [3]." According to D. Park and Yun Park, more than 25 models have been developed trying to describe kinetic behavior; however, each one of them have their own limitations. For analysis purposes, this study will use the pseudo-second order rate equation.

4.3.2.1 Pseudo-Second Order Rate Equation

The Pseudo-Second order rate equation can be defined as:

$$\frac{dq}{dt} = k_2(q_e - q)^2$$

Where, k_2 is the rate of adsorption (g/mg *min), q_e and q_e are the quantity of solute adsorbed (mg/g) at equilibrium and at time t. The linear form of the second order rate equation can be expressed as follows:

$$\frac{t}{q} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t$$

By plotting $\frac{t}{q}\ vs\ t$ we can obtain the parameters q_e and k_2 for the adsorption system. According to Ho, in his article, "Pseudo-isotherms using a second order kinetic expression constant," one of the main advantages of the pseudo second order equation is that the adsorption capacity, rate of second order, and the initial adsorption rate can be calculated using the equation without knowing any parameter [69]. Due to its versatility, the pseudo second order equation has been extensively used in the analysis of adsorption systems; however, according to Ho, the use of a linear model to express the kinetic behaviour of a system aslo brings disadvantages, such as the transformation of data which results in modifications of the error structure, alterations of the independent variable, and variations of the weight placed on each data point [69, 70, 71, 72].

Chapter 5

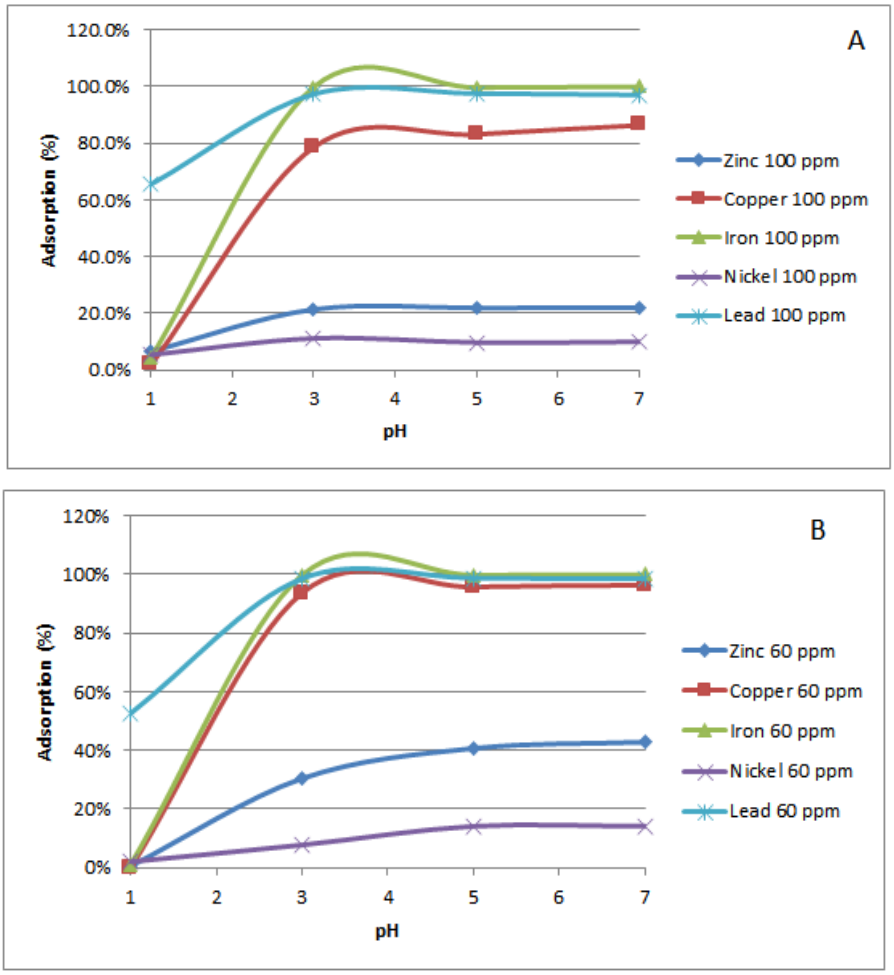
5. Results and Discussion

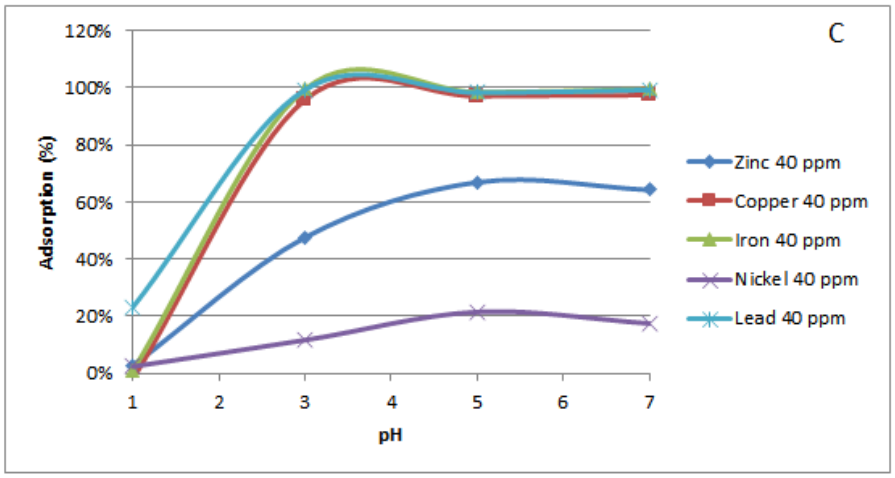
5.1 Adsorption behavior of the metal mixture as a function of the pH.

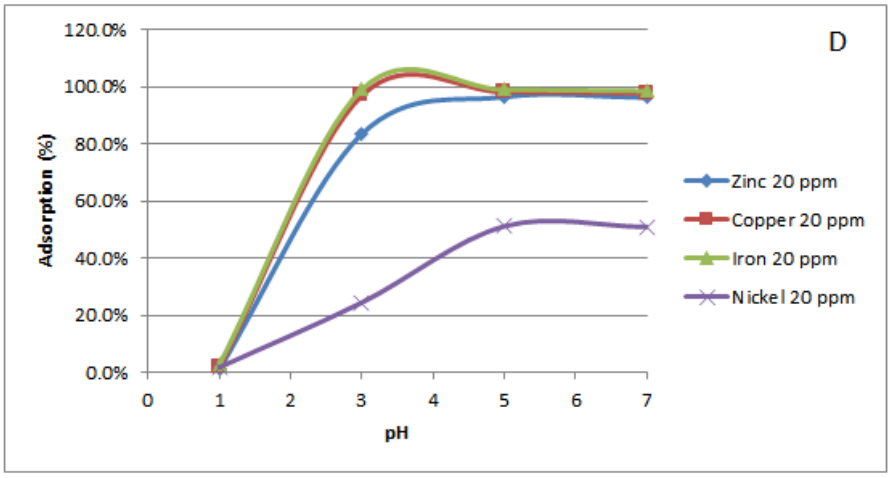
5.1.1 Standard analysis

Figure 5.1 shows the percentage adsorption of various metal ions on lobster biomass at 100, 60, 40, and 20 ppm at room temperature.

Figure 5.1. Percentage adsorption for different metal ions as a function of pH. (Room temperature) (A) 100 ppm; (B) 60 ppm; (C) 40 ppm; and (D) 20 ppm.







The % adsorption of heavy metal ions investigated in this experiment was found to increase with increasing pH in the range of 1 to 7. Figure 5.1 shows a high selectivity of the present adsorbent for iron, lead, and copper at 100, 60, 40, and 20 ppm. Figure 5.1 (A) shows that the percentage adsorption for lead and iron at 100 ppm was almost 100%, whereas the percentage adsorption for copper was above 80%. Zinc and nickel show low % adsorption with values around 20% and 10%, respectively.

Figure 5.1 (B) and (C) show that iron, lead, and copper present a remarkable selectivity of the bio-sorbent at 60 and 40 ppm. Zinc and Nickel presents once again low percentage adsorption compared with the other three metals analyzed.

Figure 5.1 (D) shows the same trend as those at 100, 60, and 40 ppm for the adsorption of iron, lead and copper; however, the % adsorption for zinc and nickel changed considerably. The % adsorption of zinc and nickel increases at lower solute concentrations. This can be explained by the number of available sites on the surface of the adsorbent. For example, at 100 ppm the adsorbent can fix on its surface a certain amount of metalic ions; however, due to a finite amount of available sites on the surface compared with the number of metalic ions present in the solution at 100 ppm, the adsorbent became saturated, and as a consequence, the % adsorption of nickel and zinc is lower than the % adsorption at 20 ppm. Thus, at lower concentrations, the percentage adsorption increases as a result of a lower concentration of metalic ions in the solution compared with the number of available sites in the adsorbent.

Also, it is important to mention that the pH appears to be the most influencing factor of the adsorption process. The pH affects considerably the solution chemistry of the metal ions in the solution [3]. In general, increments of pH values benefit the adsorption removal of cationic metals.

For all the metals ions analyzed in this study, Zn(II), Cu(II), Fe(II), Ni(II), and Pb(II), a large improvement in the adsorption capacity of metal ions was observed with increments in pH. Similar adsorption behaviour with variation in solution pH has been reported in literature [3].

In acidic conditions, where the number of protons is higher than in basic conditions, H^+ and metallic ions ($Zn^{2+}, Fe^{2+}, Ni^{2+}, Pb^{2+}, and\ Cu^{2+}$), compete for the binding of the amino groups present in the structure of chitin, and as a consequence, the % adsorption of metallic ions in solution is affected; however, with increases in pH, the amount of protons in solution became reduced, resulting in improvements in the adsorption recovery of metallic ions from aqueous solutions. This can be seen in the Figure 5.1, where, for all the metal studied, the % adsorption notably increases with increasing values of pH.

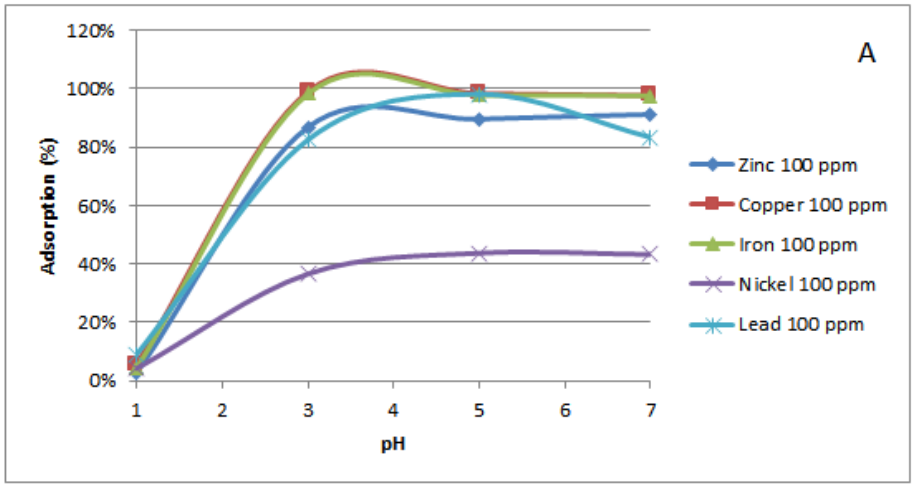
On the other hand, due to the fact that the solution analyzed was a metal mixture, competence between metal ions was presented, and as a result, the % adsorption to recover the different heavy metals in solution was also affected. In other words, the bio-sorbent shows higher selectivity for iron, lead, and copper than for zinc and nickel as a consequence of the competition of metallic ions in the solution.

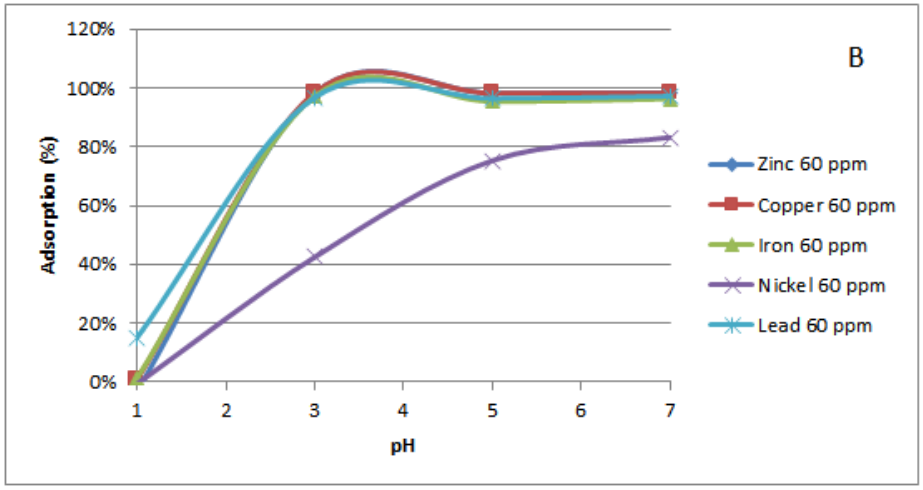
According to the results, we can conclude that the recovery of heavy metals, such as lead, iron and copper, by using lobster biomass, is effective at pH values higher than three. Lead, iron and copper were mostly recovered in acidic conditions, whereas nickel and zinc show lower % adsorption due to the saturation of the adsorbent by the metal mixture.

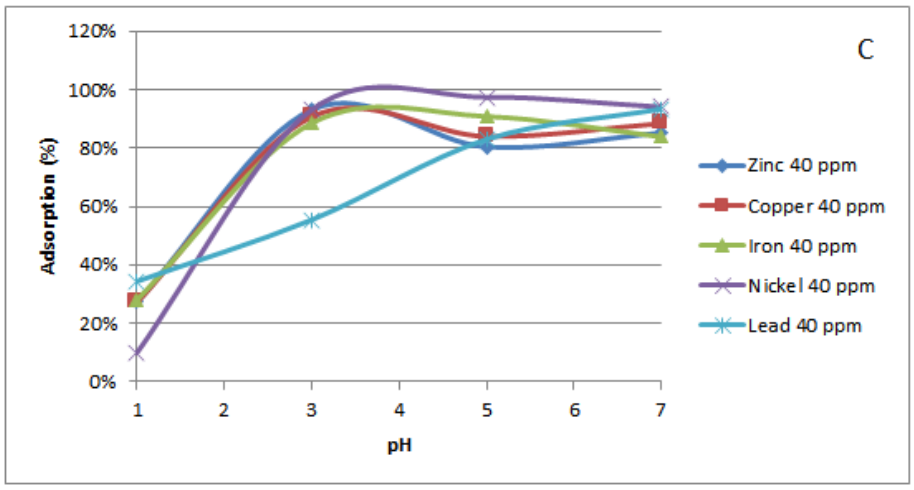
5.1.2 0 °C analysis

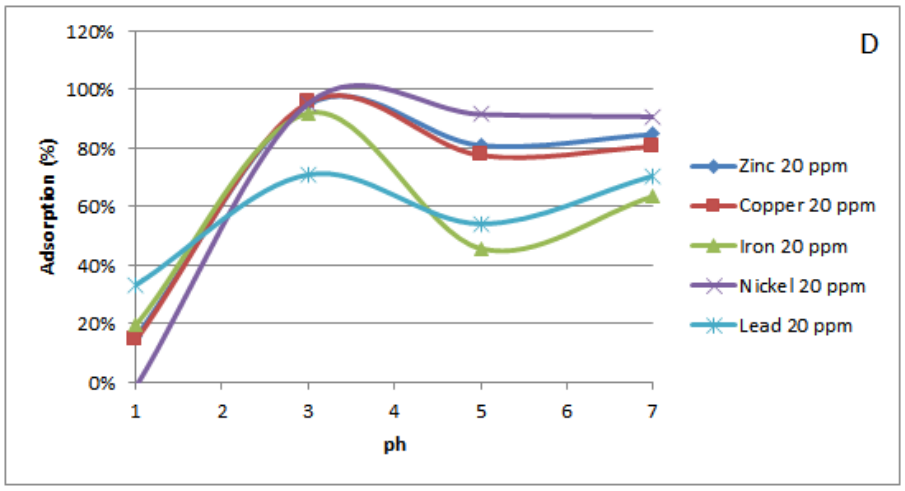
Figure 5.2 shows the percentage adsorption of various metal ions on lobster biomass at 100, 60, 40, and 20 ppm at 0 °C.

Figure 5.2. Percentage adsorption for different metal ions as a function of pH. (0 °C) (A) 100 ppm; (B) 60 ppm; (C) 40 ppm; and (D) 20 ppm.









The % adsorption of metal ions investigated in this experiment at 0 °C was found to increase with increasing pH in the range of 1 to 7, except in concentrations of 20 ppm at pH 5 for all metal ions, where the percentage adsorption decreases considerably. Figure 5.2 shows a good selectivity of the present adsorbent for iron, zinc, lead, and copper at 100, 60, 40, and 20 ppm. Figure 5.2 (A) shows that the percentage adsorption for iron, lead, zinc, and copper at 100 ppm was above 80%, whereas the percentage adsorption for nickel was close to 45% at pH-7. Figure 5.1 (B) presents a similar situation to the situation at 100 ppm; however, at 60 ppm, iron, lead, and copper present a remarkable selectivity of the bio-sorbent with % adsorption close to 100%. Additionally, although the % adsorption of nickel is lower than the other four metals analyzed, the percentage adsorption increases from 43% to 83% in concentrations of 100 and 60 ppm respectively.

Figure 5.1 (C) exhibits a similar trend in the adsorption of zinc, copper, iron, and lead; however, at 40 ppm, nickel presents a remarkable % adsorption higher than the other four metals analyzed. The percentage adsorption of nickel at pH-7 is 94% compared with the 93%, 88%, 85%, and 84% for lead, copper, iron, and zinc respectively.

Figure 5.1 (D) shows the same trend as that at 100, 60, and 40 ppm for the adsorption of iron, lead, zinc, and copper at pH-3; however, the % adsorption for all metals decreases considerably at pH-5. The % adsorption for all metals analyzed increases from pH-1 to pH-3, decreases from pH-3 to pH-5, and finally from pH-5 to pH-7 starts increasing once again with a final % adsorption of 85%, 81%, 64%, 91%, and 71% for zinc, copper, iron, nickel, and lead, respectively. Additionally, the adsorption behavior of nickel increases at lower solute concentrations (20ppm). This can be explained by the fact that, at low solute concentrations, the percentage adsorption increases as a result of a lower concentration of metallic ions in the solution compared with the number of available sites in the adsorbent. In other words, the adsorbent is saturated at higher concentrations, and as a consequence, the % adsorption for nickel increases at lower solutes concentrations of the metal mixture.

It is important to mention that at 0 °C, the pH also appears to be the most influencing factor of the adsorption process. From Figure 5.2, we can observe that increments in pH values benefit the adsorption removal of cationic metals. In other words, a large decline in the adsorption capacity of metal ions was observed at 0 °C with increments in pH, especially at pH- 3 and pH- 7.

Moreover, due to the competence between metal ions in the solution, the % adsorption of different heavy metals was also affected. Thus, we can conclude that the bio-sorbent presents higher selectivity for iron, lead, copper, and zinc than for nickel at 0°C.

Based on the results shown in Figure 5.2, we can conclude that the recovery of heavy metals, by using lobster biomass, is effective for zinc, iron, lead, and copper at pH-3 and pH-7 in

concentrations of 100, 60, 40, and 20 ppm. Results are also significant for nickel at lower solute concentrations (20 ppm) at pH-3 and pH-7.

5.2 Comparison analysis

5.2.1 Zinc adsorption (%)

Table 5.1. Comparison of room temperature and 0 °C adsorptions for zinc at different concentrations as a function of pH.

		pH-1	pH-3	pH-5	pH-7
25 °C	Zinc 100 ppm	6.7%	21.5%	22.0%	22.1%
	Zinc 60 ppm	0.6%	30.5%	40.8%	42.9%
	Zinc 40 ppm	2.8%	47.6%	67.0%	64.3%
	Zinc 20 ppm	1.3%	83.5%	96.5%	96.3%
0°C	Zinc 100 ppm	2.7%	86.9%	89.6%	91.2%
	Zinc 60 ppm	-3.1%	98.3%	98.3%	98.4%
	Zinc 40 ppm	27.2%	93.2%	80.4%	85.3%
	Zinc 20 ppm	15.5%	95.0%	81.0%	84.8%

Based on the results shown in the Table 5.1, we can observe that the recovery of heavy metal ions from aqueous solutions at room temperature and at 0 °C is significant, especially at pH 3, 5, and 7 where the % adsorption is considerably higher than at pH-1. Additionally, from Table 5.1, we can conclude that the percentage adsorption of zinc, for different values of pH, is higher at 0 °C than at room temperature. According to D. Park and Yun Park, "temperature seems to affect biosorption to a lesser extent within the range from 20 to 35 °C [3]"; however, it is important to note that no test has been performed until now trying to analyze the adsorption behaviour of metallic ions in aqueous solutions at 0 °C, and as a consequence, no literature is available that supports these results.

Moreover, from Table 5.1 we can also observe that the percentage adsorption of zinc at different values of pH is considerably higher at lower solute concentrations, as a consequence of the adsorbent's saturation at higher solute concentrations. The latter conclusion is in accordance with D. Park and Yun Park, in their article, "The Past, Present, and Future Trends of Biosorption," where they mention that higher initial concentrations, increases the quantity of biosorbed pollutant per unit weight of biosorbent, but [also] decreases its removal efficiency [3]."

5.2.2 Copper adsorption (%)

Table 5.2. Comparison of room temperature and 0 °C adsorptions for copper at different concentrations as a function of pH.

		pH-1	pH-3	pH-5	pH-7
25 °C	Copper 100 ppm	1.9%	78.7%	83.2%	86.4%
	Copper 60 ppm	0.0%	93.7%	95.8%	96.4%
	Copper 40 ppm	-2.0%	95.8%	97.1%	97.5%
	Copper 20 ppm	2.0%	97.0%	98.2%	97.7%
0°C	Copper 100 ppm	5.7%	99.0%	98.4%	97.7%
	Copper 60 ppm	0.8%	98.4%	98.3%	98.3%
	Copper 40 ppm	27.2%	90.8%	84.0%	88.5%
	Copper 20 ppm	14.3%	95.6%	77.5%	80.6%

Table 5.2 shows the comparison between room temperature and 0 °C adsorptions for copper at different concentrations. From Table 5.2, we can observe that the recovery of copper ions from aqueous solutions at room temperature and at 0 °C is substantial, especially at pH 3 and 7, where the % adsorption is considerably higher than at pH-1. The lowest pH analyzed, pH-1, presents almost no recovery of copper at room temperature for all the concentrations. In contrast, the recovery of copper at pH-1 and 0 °C shows higher % adsorption than at room

temperature, but lower than at pH-3, 5, and 7 in the same temperature for all the concentrations.

Moreover, from Table 5.2 we can observe that the % adsorption of zinc at 60 ppm is the optimal concentration for adsorption at the different values of pH with the exception of pH-1. The % adsorption of copper in initial concentrations of 60 ppm at room temperature is 93.7%, 95.8%, and 96.4% for pH 3, 5, and 7 respectively. On the other hand, the % adsorption at 0 °C of copper in concentrations of 60 ppm is 98.4%, 98.3%, and 98.3% for pH 3, 5, and 7, respectively.

5.2.3 Iron adsorption (%)

Table 5.3. Comparison of room temperature and 0 °C adsorptions for iron at different concentrations as a function of pH. Source:

		pH-1	pH-3	pH-5	pH-7
25 °C	Iron 100 ppm	4.5%	99.9%	99.7%	100.0%
	Iron 60 ppm	1.1%	99.8%	99.8%	100.0%
	Iron 40 ppm	1.0%	99.5%	98.5%	99.5%
	Iron 20 ppm	2.8%	99.1%	99.0%	98.6%
0°C	Iron100 ppm	4.3%	98.3%	97.8%	97.6%
	Iron 60 ppm	1.3%	97.3%	95.5%	96.3%
	Iron 40 ppm	28.1%	88.6%	90.9%	83.9%
	Iron 20 ppm	19.5%	92.0%	45.7%	63.6%

Table 5.3 shows the comparison between room temperature and 0 °C adsorptions for iron at 100, 60, 40, and 20 ppm. From Table 5.3, we can conclude that the adsorption of iron ions from aqueous solutions at room temperature and at 0°C is considerably important at pH 3, 5, and 7. The % adsorption of iron is above 90% for most of the concentrations with the

exception of iron at 20 ppm and 0 °C., where the adsorption is 45.7% and 63.6% for pH-5 and 7, respectively.

As mentioned before, the adsorption of metal ions from aqueous solutions is significantly affected by the pH value of the solution, especially at pH-1, where the % adsorption of iron is negatively impacted at room temperature and at 0 °C. This situation can be seen in Table 5.3

Additionally, from Table 5.3, we can conclude that the percentage adsorption of iron at different concentrations and for different values of pH, with the exception of pH-1, is higher at room temperature than at 0 °C. This can be explained by the fact that most of bio-sorptive systems are endothermic, and as consequence higher temperatures enhance the adsorbent's surface activity and increase the kinetic energy [3]. Nevertheless, higher temperatures can also affect the physical structure of the adsorbent; thus, room temperatures are recommended for adsorption systems.

It is important to note that the emphasis of this study is based on the recovery of copper, zinc, lead, iron, and nickel from wastewater laden with heavy metals at low temperatures in Newfoundland and Labrador. Results have proven to be positive using crab biomass for temperatures ranging from 20 to 35 °C; however, no test has been performed to measure the recovery at low temperatures.

5.2.4 Nickel adsorption (%)

Table 5.4. Comparison of room temperature and 0 °C adsorptions for nickel at different concentrations as function of pH. Source:

		pH-1	pH-3	pH-5	pH-7
25 °C	Nickel 100 ppm	5.5%	11.2%	9.8%	10.0%
	Nickel 60 ppm	2.1%	7.8%	14.2%	14.2%
	Nickel 40 ppm	2.5%	11.7%	21.6%	17.5%
	Nickel 20 ppm	1.9%	24.5%	51.2%	51.0%
0°C	Nickel 100 ppm	4.2%	36.6%	43.7%	43.2%
	Nickel 60 ppm	-0.7%	42.5%	75.3%	83.3%
	Nickel 40 ppm	9.9%	93.2%	97.5%	94.1%
	Nickel 20 ppm	-1.6%	95.3%	91.6%	90.8%

Table 5.4 shows the comparison between room temperature and 0 °C adsorptions for iron at 100, 60, 40, and 20 ppm as function of pH. Among all the metals analyzed in this study, nickel is the one with lower % adsorption, especially at room temperature, for the different values of pH at different concentrations.

Additionally, the adsorption behavior of nickel, at room temperature and 0 °C, increases at lower solute concentrations (40 and 20 ppm). At lower solute concentrations, the percentage adsorption increases as a result of a lower concentration of metallic ions in the solution compared with the number of available sites in the adsorbent. Thus, based on the results shown in Table 5.4, we can observe that the % adsorption of nickel notably increases from 43.2% to 90.8%, at pH-1 and 0 °C, in concentrations of 100 and 20 ppm, respectively.

In other words, at higher concentrations the adsorbent is saturated, and as a consequence, the % adsorption for nickel increases at lower solutes concentrations of the metal mixture (40 and 20 ppm).

From Table 5.4, we can also observe that the percentage adsorption of nickel at different concentrations and for different values of pH, with the exception of pH-1, is higher at 0 °C than at room temperature.

5.2.5 Lead adsorption (%)

Table 5.5. Comparison of room temperature and 0 °C adsorption for lead at different concentrations as function of pH. Source:

		pH-1	pH-3	pH-5	pH-7
25 °C	Lead 100 ppm	65.6%	97.4%	97.6%	97.1%
	Lead 60 ppm	52.7%	98.6%	98.8%	98.6%
	Lead 40 ppm	23.2%	99.4%	98.3%	99.3%
	Lead 20 ppm	41.9%	98.9%	98.2%	98.4%
0°C	Lead 100 ppm	9.0%	82.6%	98.2%	83.3%
	Lead 60 ppm	15.1%	96.8%	96.5%	97.3%
	Lead 40 ppm	34.4%	55.5%	83.0%	93.4%
	Lead 20 ppm	33.2%	71.0%	54.2%	70.6%

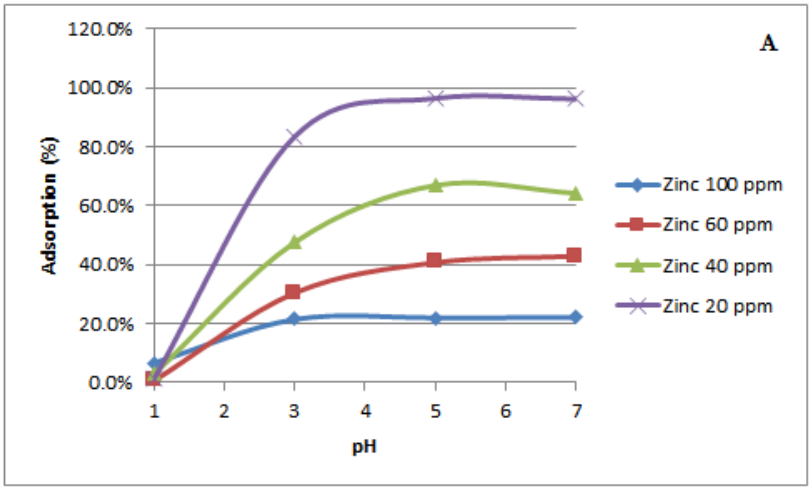
Table 5.5 shows the comparison between room temperature and 0 °C adsorptions for lead at 100, 60, 40, and 20 ppm. Among all the metals analyzed in this study, lead is the metal with the highest % adsorption, especially at room temperature, for the different values of pH at different concentrations.

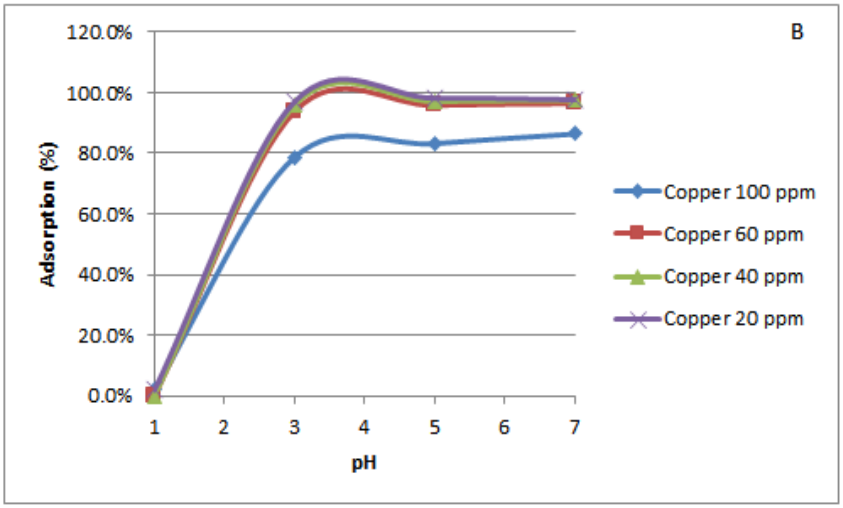
It is important to mention that lead is the only metal, which among all the metals analyzed in this study, shows significant % adsorption at pH-1. The adsorption of lead at room temperature at pH-1 is 65.6%, 52.7%, 23.2%, and 41.9% for the concentrations of 100, 60, 40, and 20 ppm, respectively. In contrast, 0 °C, the adsorption of lead at pH-1 is 9%, 15.1%, 34.4%, and 33.2% for the same concentrations.

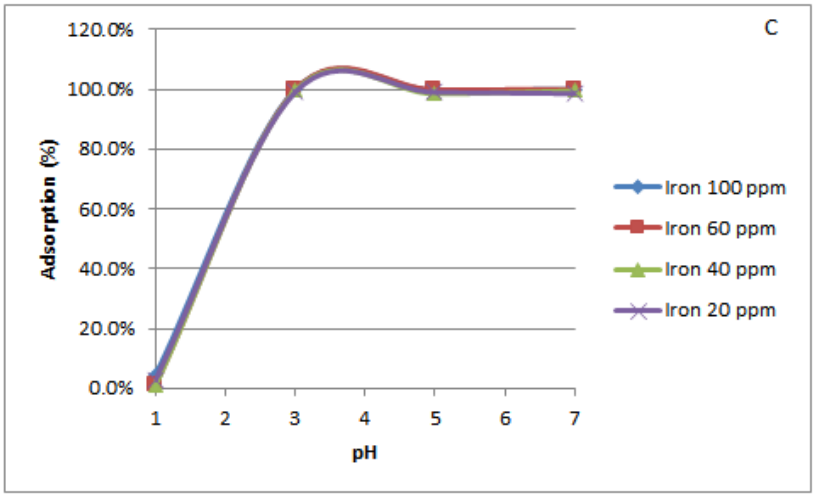
5.3 Adsorption behavior of individual metals at different values of pH.

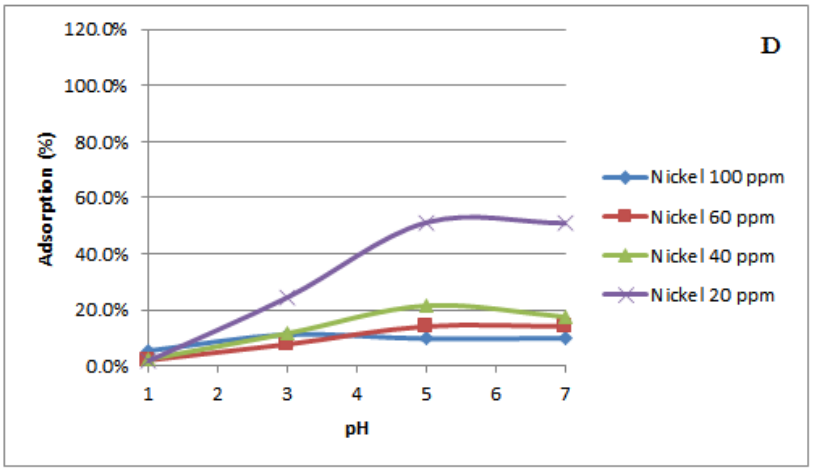
5.3.1 Standard analysis

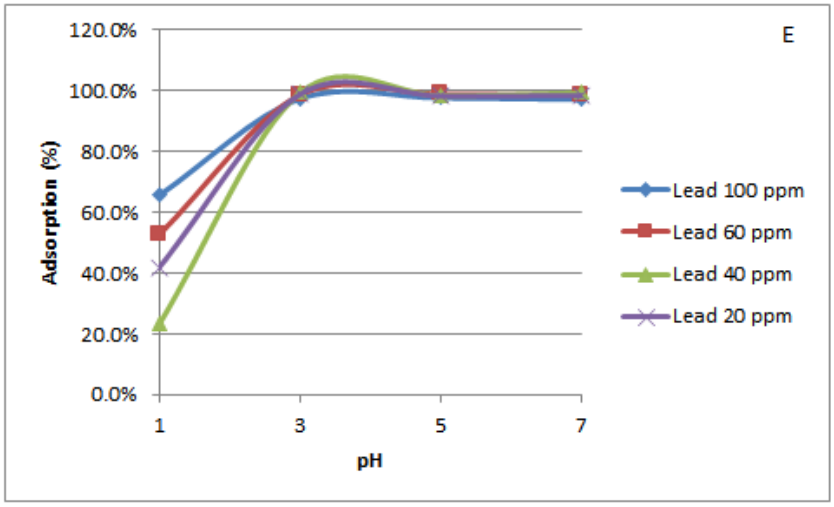
Figure 5.3. Adsorption behavior of individual metals as a function of pH at room temperature. (A) zinc; (B) copper; (C) iron; (D) nickel; and (E) lead.






C
120.0%
100.0%
80.0%
60.0%
40.0%
20.0%
0.0%
Adsorption (%)
1
2
3
4
5
6
7
pH
Iron 100 ppm
Iron 60 ppm
Iron 40 ppm
Iron 20 ppm


D
120.0%
100.0%
80.0%
60.0%
40.0%
20.0%
0.0%
Adsorption (%)
1
2
3
4
5
6
7
pH
Nickel 100 ppm
Nickel 60 ppm
Nickel 40 ppm
Nickel 20 ppm


E
120.0%
100.0%
80.0%
60.0%
40.0%
20.0%
0.0%
Adsorption (%)
1
3
5
7
pH
Lead 100 ppm
Lead 60 ppm
Lead 40 ppm
Lead 20 ppm

The adsorption behavior of individual metals investigated in this experiment was found to increase with increasing pH in the range of 1 to 7. Figure 5.3 (A) shows that the % adsorption of zinc increases at lower solute concentrations. This can be explained by the number of available sites on the surface of the adsorbent. In other words, at lower concentrations, the percentage adsorption increases as a result of a lower concentration of zinc ions in the solution compared with the number of available sites in the adsorbent.

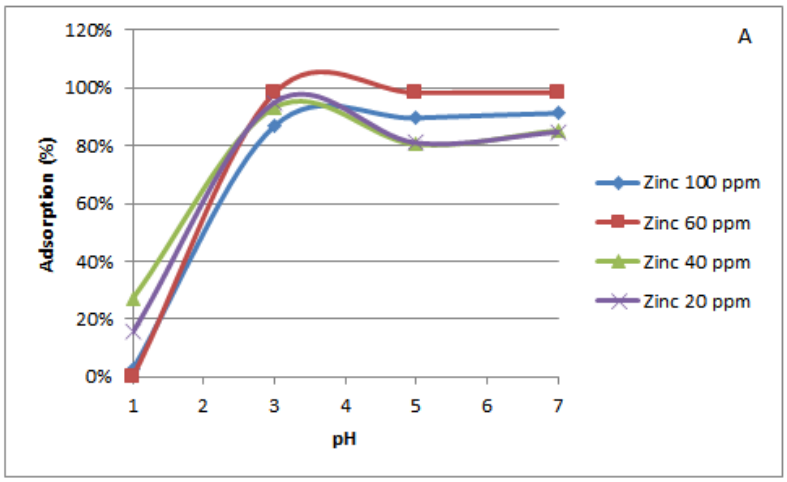
Figure 5.3 (B) shows almost complete adsorption of copper ions in the different metal concentrations, except for copper ions at 100 ppm, where the % adsorption is approximately 85%. Consequently, we can conclude that the present adsorbent shows a high selectivity for copper at 100, 60, 40, and 20 ppm.

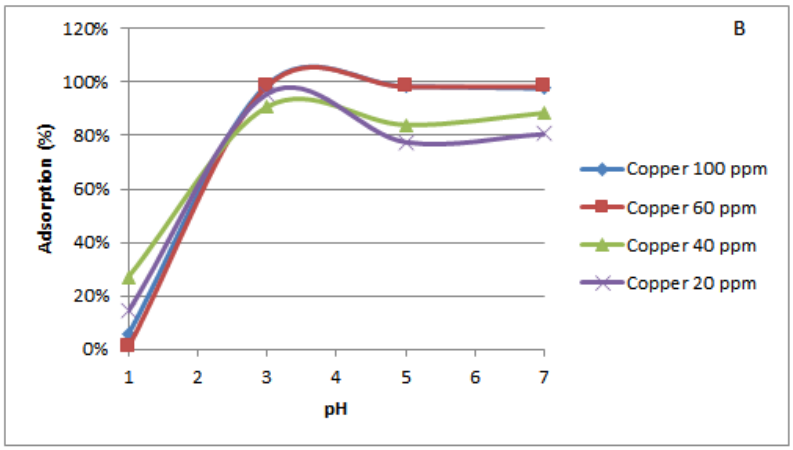
Figure 5.3 (C) and (E) exhibit a similar trend in the adsorption of iron and lead; however, it is important to mention that the % adsorption of iron and lead is higher than zinc at all concentrations analyzed. It is also important to note that lead ions are significantly recovered from aqueous solutions at pH-1, whereas all the other metals analyzed in this study show almost zero affinity for the present adsorbent at the same pH.

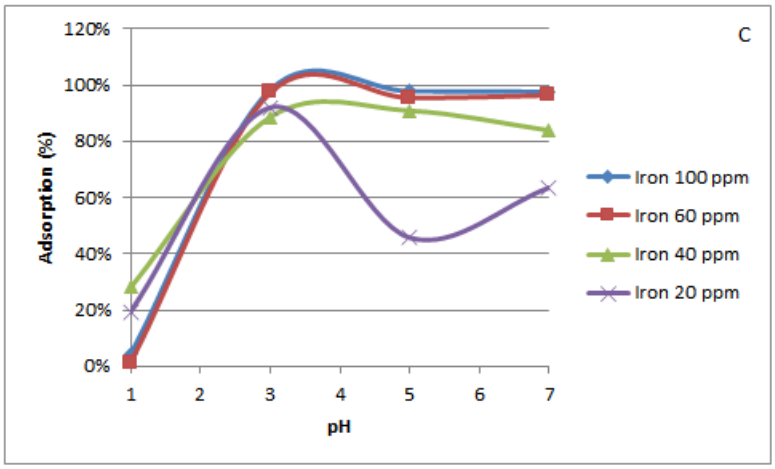
Figure 5.3 (D) presents the lowest adsorption values among all the metals studied. The highest adsorption of nickel ions occurred at 20 ppm with a % adsorption close to 50%; however, for all the other concentrations, 40, 60, 80, and 100 ppm, the % adsorption is lower than 20% at the different values of pH. This can be explained by the fact that higher initial concentrations increase the amount of solute adsorbed per unit weight of biosorbent, but also decreases the removal efficiency of the adsorbent [3].

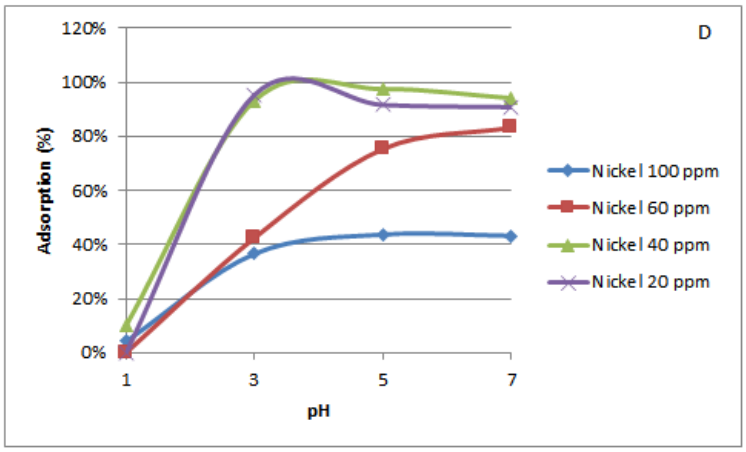
5.3.2 0 °C analysis

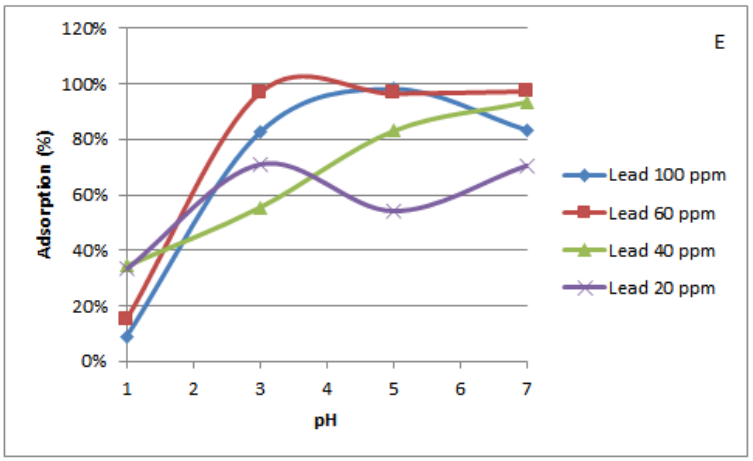
Figure 5.4. Adsorption behavior of individual metals as a function of pH at 0 °C (A) zinc; (B) copper; (C) iron; (D) nickel; and (E) lead.











The adsorption behavior of individual metals analyzed in this experiment was found to increase with increasing pH in the range of 1 to 7. Figure 5.4 (A) and (B) shows a similar trend where the highest and the lowest % adsorption for zinc and copper occur at 60 and 20 ppm, respectively.

Figure 5.4 (C) and (E) also show a similar adsorption behavior for the metal ions iron and lead. The adsorption behavior for lead and iron presents a remarkable adsorption in concentrations of 40, 60, and 100 ppm with the exception of 20 ppm where the % adsorption is close to 70%. It is important to mention that, even though at 20 ppm the % adsorption of

iron and lead is lower than at higher metallic concentrations, the adsorption behavior of these two metals leads to the conclusion that iron and lead can be easily recovered from aqueous solutions, with the use of lobster biomass, in order to treat wastewater laden with heavy metals at low temperatures in Newfoundland and Labrador.

Figure 5.4 (D) shows that the % adsorption of nickel at 0 °C increases at lower solute concentrations. This statement can be explained by the number of available sites on the surface of the adsorbent. Thus, at lower concentrations, the % adsorption increases as a result of a lower concentration of nickel ions in the solution compared with the number of available sites in the surface of the adsorbent. Also it can be explained by the fact that "higher initial concentrations, increases the quantity of biosorbed pollutant per unit weight of biosorbent, but [also] decreases its removal efficiency [3]."

5.4 Adsorption Isotherms

5.4.1 Langmuir isotherm analysis

Langmuir isotherm analysis was examined with the intention of fitting experimental data for the different metals ions used in this study. It is important to mention that effluents from industries, such as mining, metal processing, finishing, and plating, contain different soluble heavy metals that pose a risk for the environment. Thus, it is usually required to treat wastewater in order to prevent and control the deposition of toxic pollutants into soil and water sources [74, 75]. Wastewater from mining facilities, containing several metals, need to be analyzed as a mixture in order to identify the adsorption of different pollutants. Extensive literature has shown that the adsorption of individual heavy metals is possible by using

different adsorbents; however, in order to simulate real conditions, where different metal ions are present in wastewater, a metal mixture was used in this study with the purpose of determining the adsorption of different heavy metals.

Table 5.6. Langmuir parameters for zinc, copper, iron, nickel, and lead.

Langmuir				
		b (L/mg)	qm (mg/mg)	R2
Zinc pH-1	(25°C)	0.00051	0.02702	0.4738
	(0°C)	-0.02114	-0.00686	0.13
Zinc pH-3	(25°C)	19.6996	0.02053	0.0076
	(0°C)	0.5197	0.0798	0.3576
Zinc pH-5	(25°C)	8.40597	0.02529	0.3216
	(0°C)	-2.78856	0.02872	0.0527
Zinc pH-7	(25°C)	10.3895	0.0257	0.2002
	(0°C)	-3.74108	0.03061	0.0309

Langmuir				
		b (L/mg)	qm (mg/mg)	R2
Copper pH-1	(25°C)	-0.0172	-0.00098	0.442
	(0°C)	-0.07582	0.00092	0.1141
Copper pH-3	(25°C)	0.47809	0.08908	0.9999
	(0°C)	5.8389	0.04299	0.0075
Copper pH-5	(25°C)	0.80889	0.08909	0.9988
	(0°C)	-1.22371	0.01967	0.4283
Copper pH-7	(25°C)	0.46614	0.11443	0.9922
	(0°C)	-1.39796	0.0225	0.247

Langmuir				
		b (L/mg)	qm (mg/mg)	R2
Iron pH-1	(25°C)	0.03024	0.00126	0.2227
	(0°C)	-0.08175	0.00133	0.1478
Iron pH-3	(25°C)	-11.8956	0.01651555	0.6376
	(0°C)	4.6961	0.04035675	0.0028
Iron pH-5	(25°C)	-58.0503	0.03615198	0.0093
	(0°C)	-0.446455	0.00808996	0.8851
Iron pH-7	(25°C)	3.7693119	0.06219679	0.3929
	(0°C)	-0.531379	0.01329116	0.5973

Langmuir				
		b (L/mg)	qm (mg/mg)	R2
Nickel pH-1	(25°C)	-0.006552	-0.0025209	0.9845
	(0°C)	-0.00446	0.00375728	0.3255
Nickel pH-3	(25°C)	0.1322428	0.00715001	0.1787
	(0°C)	1.6030853	0.03376439	0.566
Nickel pH-5	(25°C)	-0.843286	0.00917263	0.4512
	(0°C)	2.269481	0.03781576	0.1194
Nickel pH-7	(25°C)	-0.69679	0.00848	0.1342
	(0°C)	0.34087	0.05757	0.6356

Langmuir				
		b (L/mg)	qm (mg/mg)	R2
Lead pH-1	(25°C)	-0.01032	-0.04297	0.683
	(0°C)	0.1464	0.01121	0.2959
Lead pH-3	(25°C)	0.98708	0.13582	0.7635
	(0°C)	0.16487	0.04652	0.1079
Lead pH-5	(25°C)	-0.12107	-0.45645	0.9849
	(0°C)	-0.18048	0.00464	0.9201
Lead pH-7	(25°C)	0.51312	0.18361	0.6763
	(0°C)	2.35346	0.03403	0.0039

From Table 5.6, we can observe the different Langmuir parameters determined with the experimental data obtained from the test. Due to the complexity of the adsorption system analyzed, the Langmuir parameters, b and q_m, seem to not fit the experimental data for the different metal ions studied. For instance, iron ions at pH 3, 5, and 7 did not fit the Langmuir isotherm, "giving negative slopes and intercepts, leading to the conclusion that the adsorption behavior of the tested systems does not follow the assumption on which the Langmuir approach is based [73]."

Additionally, from Table 5.6, we can observe that for different parameters calculated, the R^2 is not significantly high enough to conclude that the experimental data fits the Langmuir isotherm.

The latter conclusion can be observed for all the metals studied at room temperature and at 0 °C. According to Carvalho, Abreu, Benachour, Sales, Barauna, and Sobrinho, in their article "Applying Combined Langmuir–Freundlich Model to the Multi-Component Adsorption of BTEX and Phenol on Smectite Clay," due to the complexity of different multicomponent systems, "there is no specific model that can universally be applied to such systems [65]".

Furthermore, according to Giles, MacEwan, Nakhwa, and Smith, the adsorption of multicomponent systems tends to behave differently, due to the fact that "with [the] increase in the proportion of one component of the mixture the isotherm reaches a maximum and then descends [76]." This behavior can be seen in most of the metals studied, and as a consequence, the experimental data cannot be fitted to an ideal model, such as the Langmuir Isotherm.

5.4.2 Freundlich isotherm analysis

Freundlich isotherm analysis was examined with the intention of fitting experimental data for the different metals ions used in this study. As mentioned before, in order to simulate the real conditions, where different metal ions are present in wastewater, a metal mixture was used in this study with the purpose of determining the adsorption of different heavy metals ions.

Table 5.7. Freundlich parameters for zinc, copper, iron, nickel, and lead

Freundlich				
		n	K (mg/mg)	R2
Zinc pH-1	(25°C)	0.564971	1.02E-06	0.5510
	(0°C)	1.0409077	4.85E-04	0.0727
Zinc pH-3	(25°C)	59.52381	2.02E-02	0.8845
	(0°C)	2.675943	3.11E-02	0.4749
Zinc pH-5	(25°C)	60.97561	2.34E-02	0.0685
	(0°C)	23.923445	3.84E-02	0.0034
Zinc pH-7	(25°C)	102.0408	2.44E-02	0.0280
	(0°C)	9.7276265	3.69E-02	0.0188

Freundlich				
		n	K (mg/mg)	R2
Copper pH-1	(25°C)	0.6743088	9.28E-05	0.0592
	(0°C)	-3.188775	9.82E-03	0.0318
Copper pH-3	(25°C)	2.7956388	3.00E-02	0.9041
	(0°C)	-7.057163	4.67E-02	0.0193
Copper pH-5	(25°C)	2.8727377	3.61E-02	0.8963
	(0°C)	-1.499475	7.93E-02	0.5204
Copper pH-7	(25°C)	2.4881811	3.47E-02	0.8896
	(0°C)	-1.577785	7.70E-02	0.3182

Freundlich				
		n	K (mg/mg)	R2
Iron pH-1	(25°C)	0.8388558	9.42E-06	0.5267
	(0°C)	-2.07168	2.07E-02	0.1169
Iron pH-3	(25°C)	-0.642963	2.46E-03	0.7344
	(0°C)	-4.768717	5.15E-02	0.0221
Iron pH-5	(25°C)	-30.1204	4.52E-02	0.0013
	(0°C)	-0.705866	2.56E-01	0.9858
Iron pH-7	(25°C)	1.63372	7.38E-02	0.5794
	(0°C)	-0.833959	2.05E-01	0.7643

Freundlich				
		n	K (mg/mg)	R2
Nickel pH-1	(25°C)	0.614439	2.49E-06	0.9280
	(0°C)	-0.474947	1.97E-02	0.1961
Nickel pH-3	(25°C)	2.8074116	1.63E-03	0.3966
	(0°C)	13.140604	2.42E-02	0.2283
Nickel pH-5	(25°C)	-23.7529	1.12E-02	0.2271
	(0°C)	7.806401	2.73E-02	0.3202
Nickel pH-7	(25°C)	-40.32258	9.93E-03	0.0204
	(0°C)	5.4674686	2.44E-02	0.4121

Freundlich				
		n	K (mg/mg)	R2
Lead pH-1	(25°C)	0.652912	2.28E-04	0.9486
	(0°C)	12.004802	6.91E-03	0.0535
Lead pH-3	(25°C)	1.7467249	6.03E-02	0.8944
	(0°C)	2.7019724	1.47E-02	0.0877
Lead pH-5	(25°C)	1.126253	5.45E-02	0.9264
	(0°C)	-0.232596	1.43E-02	0.9911
Lead pH-7	(25°C)	1.539883	5.47E-02	0.8501
	(0°C)	2.3052098	1.82E-02	0.1922

From Table 5.7, we can conclude the different Freundlich parameters determined with the experimental data obtained from the test. As a consequence of the multi-metal adsorption system analyzed, the Freundlich parameters, n and K, appear to not fit the experimental data for the different metal ions studied; however, compared with the results obtained from the Langmuir analysis, the Freundlich isotherm, better fits experimental data even though some values present negative affinity and uptake.

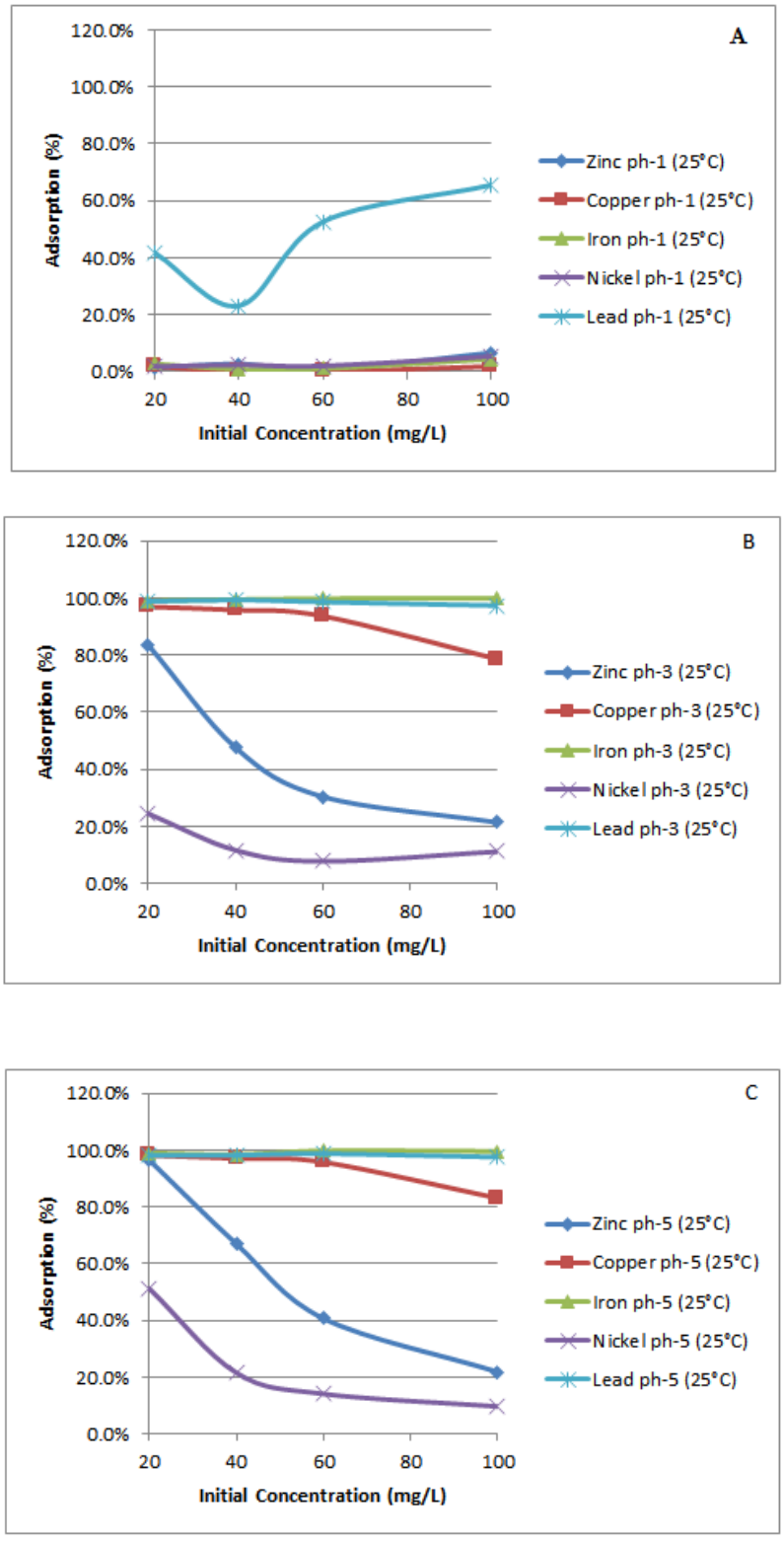
For instance, iron at pH-5, zinc at pH-3, copper at pH-3, nickel at pH-1, and lead at pH-1, seem to fit the Freundlich isotherm reasonably well; however, many other values in Table 5.7 lead to the conclusion that the experimental data cannot be explained by the Freundlich isotherm. Thus, experimental data is analyzed based on the % adsorption of each heavy metal as a function of the initial concentration of the solution.

5.4.3 Standard percentage adsorption analysis

In order to show that the adsorption behavior for the different metal ions, the adsorption analysis is based on the % adsorption for Zn, Cu, Ni, Pb, and Fe, as a function of the initial concentration of each heavy metal ion.

Figure 5.5 (A) shows the % adsorption for different metals as a function of the initial concentration at pH-1 and room temperature. This figure shows that the adsorption of zinc, nickel, copper, and iron is almost negligible, compared with the adsorption of lead, which at the same pH shows an adsorption of almost 65%.

Figure 5.5. % adsorption for different metals as a function of initial concentration at room temperature. (A) pH-1; (B) pH-3; (C) pH-5; and (D) pH-7.



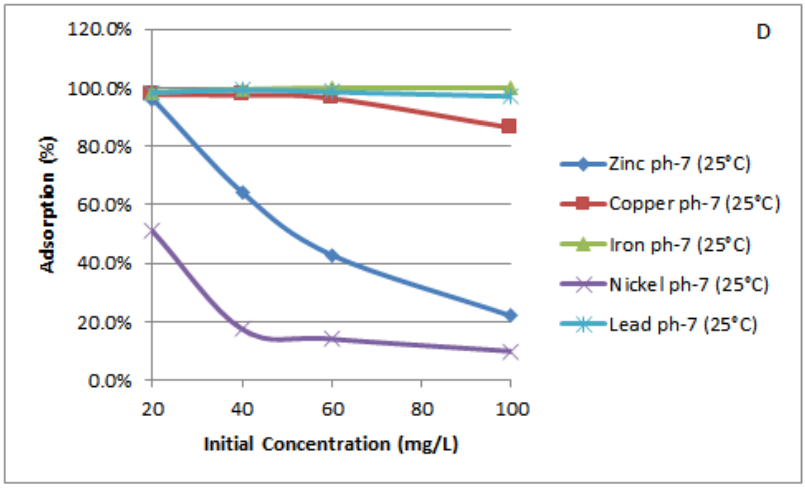
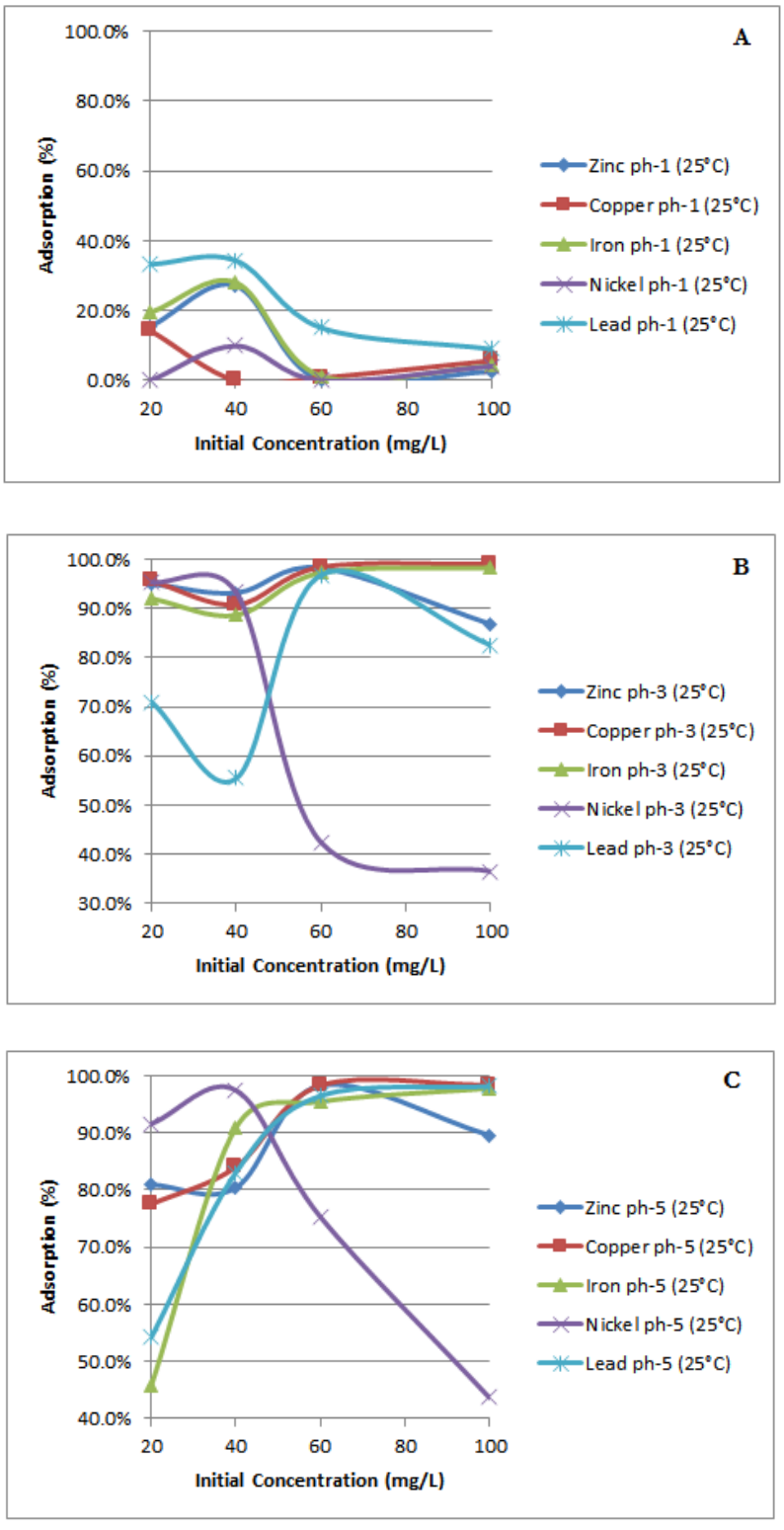


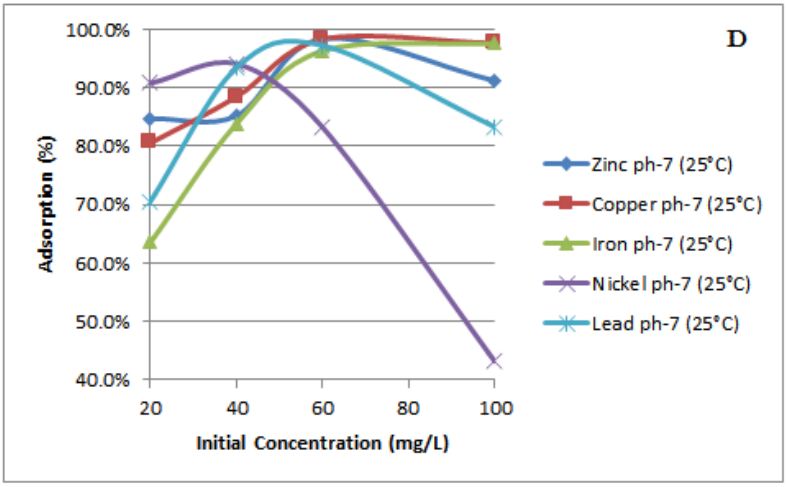
Figure 5.5 (B), (C), and (D) shows a similar trend for different pH values. Iron and lead present an adsorption of almost 100% for all the solute concentrations, compared with nickel and zinc whereby the % adsorption decreases with increments in solute concentrations. In other words, iron and lead are almost completely adsorbed by the lobster biomass in all concentrations analyzed (20 to 100 ppm), while the % adsorption of nickel and zinc decreases as a consequence of increments in the solute concentrations from 20 to 100 ppm. It is important to mention that with the exception of iron and lead, the adsorption of heavy metals at low concentrations is more efficient than at higher concentrations. This can be explained once again by saturation of the adsorbent at higher concentrations.

It is also important to note that although the Langmuir and Freundlich isotherm models cannot be fitted to the experimental data, it can be seen from Figure 5.5 that the adsorption of heavy metals ions at room temperature is absolutely possible, especially for iron, lead, and copper at pH 3, 5, and 7, to treat wastewater present in discharge points from mining facilities in Newfoundland and Labrador.

5.4.4 0 °C percentage adsorption analysis

Figure 5.6. % adsorption for different metals as a function of initial concentration at 0 °C. (A) pH-1; (B) pH-3; (C) pH-5; and (D) pH-7





In order to analyze the adsorption behavior of the lobster biomass at 0 °C, which is the main purpose of this study, the % adsorption of Zn, Cu, Ni, Pb, and Fe was plotted as a function of the initial concentration of each heavy metal ion.

Figure 5.5 (A) shows that the % adsorption decreases with increments in concentrations at pH-1 for all heavy metal ions analyzed. For instance, at 100 ppm, the % adsorption of all metallic ions is close to 5% due to the saturation of the adsorbent; however, with the exception of nickel, the % adsorption at 20 ppm increases to 15, 15, 20, and 33% for copper, zinc, iron, and lead respectively.

Figure 5.5 (B), (C), and(D) shows that for metals, such as lead and copper, the % adsorption increases with increments in concentrations from 20 to 60 ppm, but from 60 to 100 ppm the % adsorption is reduced. The latter conclusion is valid for lead and copper ions at pH-3, 5, and 7. Additionally, from Figure 5.5 (B), (C), and (D), we can observe that the % adsorption of nickel is notably reduced with increments in the solution's concentration. For instance, at 100 ppm, the % adsorption of nickel is close to 40%, whereas at 20 ppm, the percentage adsorption is close to 90% at pH 3, 5, and 7.

It is important to mention that in order to prove, the effectiveness of the adsorbent at 0 °C, which is the main purpose of this study, several tests are performed and analyzed to describe the sorption behavior of the adsorbent. Thus, based on the results of Figure 5.5, we can conclude that the adsorption of heavy metals ions at 0 °C is completely possible, especially for iron, lead and copper and zinc at pH 3, 5, and 7.

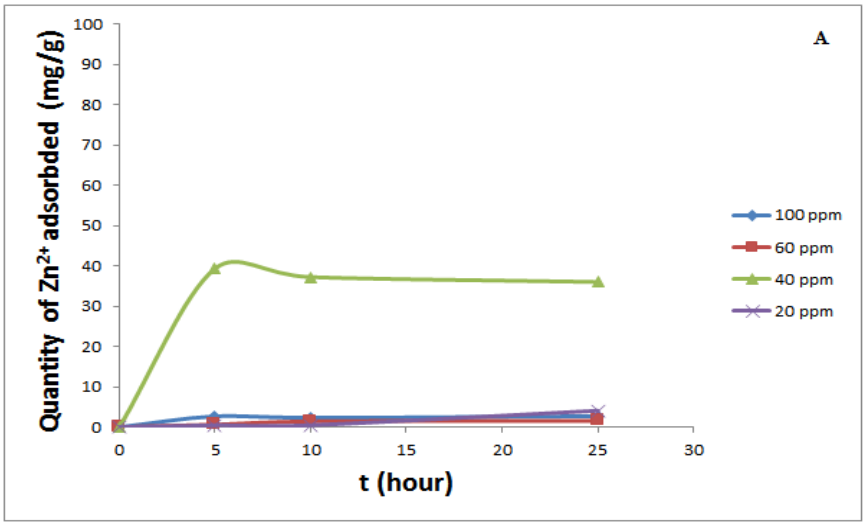
5.5 Adsorption Kinetics

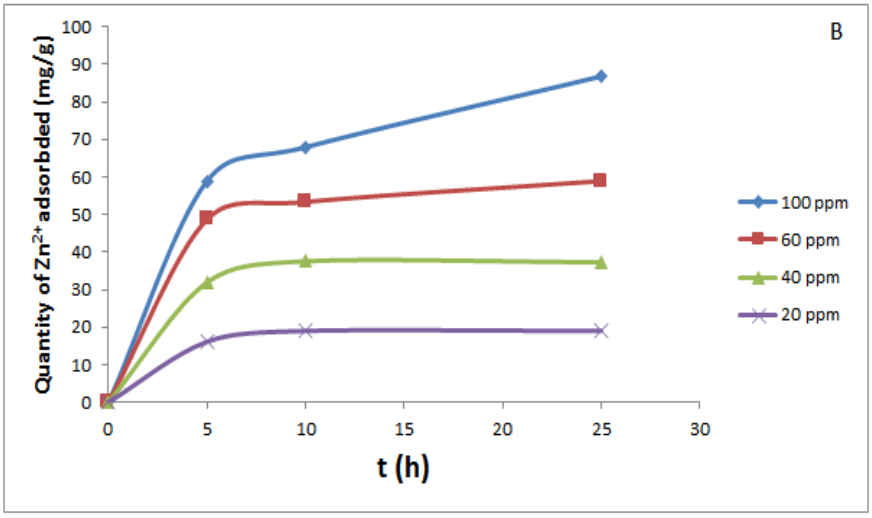
5.5.1 Effect of contact time on adsorption behavior

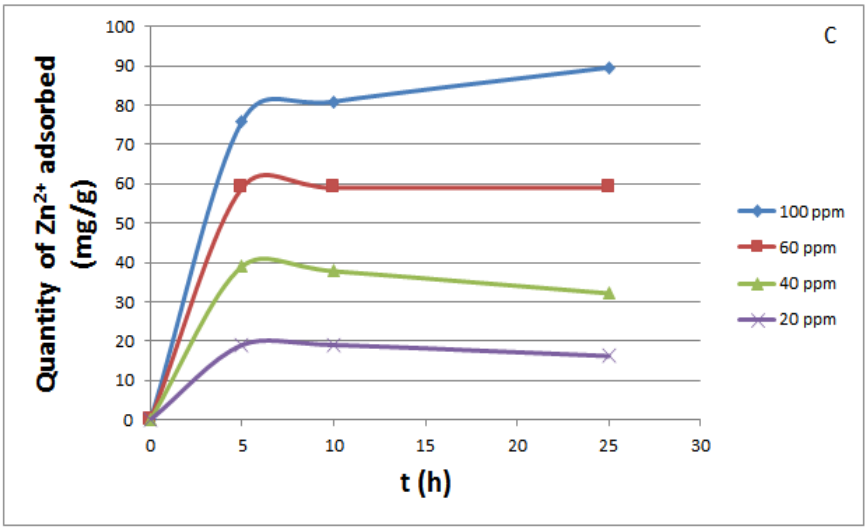
The adsorption process of heavy metal ions by chitin can be studied by monitoring the effect of time during the adsorption process to determine the adsorption equilibrium of each metal ion at different pH values. The effect of contact time on the adsorption of metal ions by chitin was investigated for 25 hours at different pH (1, 3, 5, and 7) and at different initial concentrations of metal (100 ppm, 60 ppm, 40 ppm, and 20 ppm) at 0 °C. It is important to mention that all experiments are performed with a shaking speed of 115 rpm.

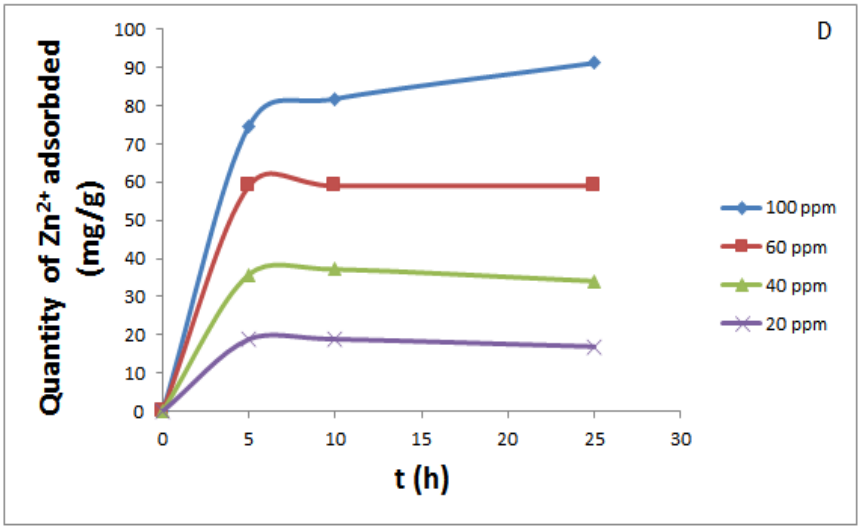
5.5.1.1 Effect of contact time on adsorption behavior of zinc at 0 °C

Figure 5.7. Effect of contact time on the adsorption of zinc ions at different initial concentrations and pH values. (A) pH 1, (B) pH 3, (C) pH 5, and (D) pH 7




B
Quantity of Zn2+ adsorbded (mg/g)
t (h)
100 ppm
60 ppm
40 ppm
20 ppm

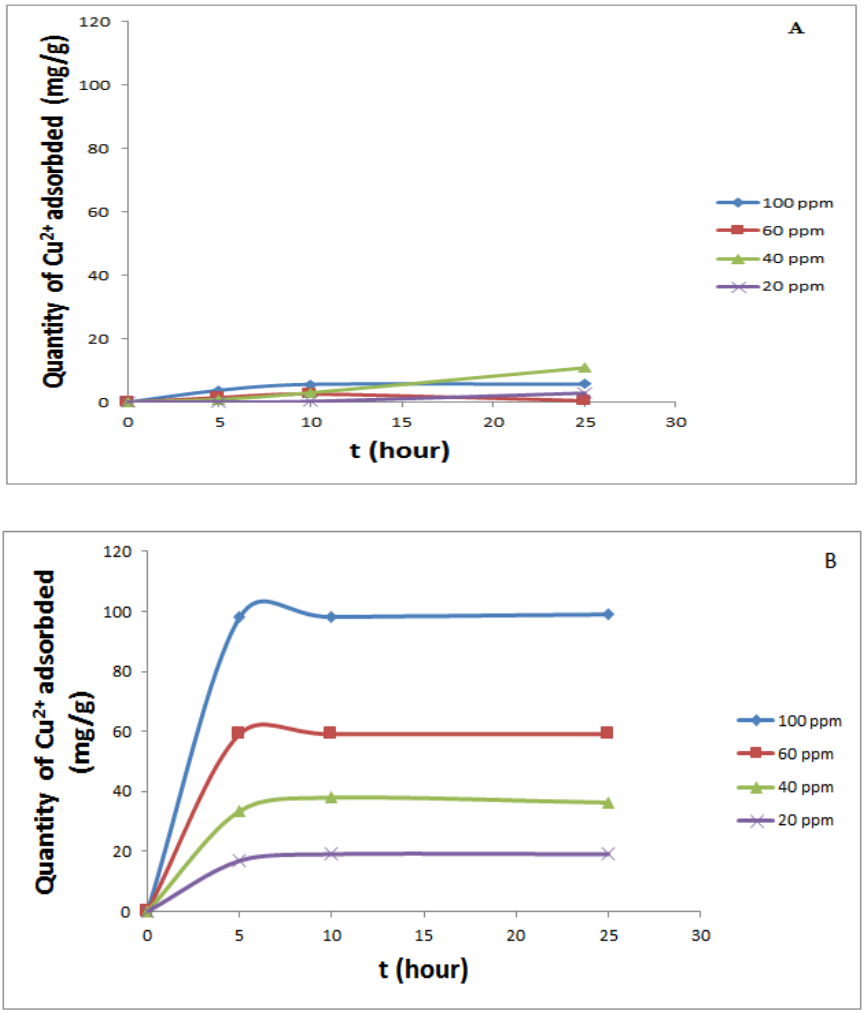

C
Quantity of Zn2+ adsorbed (mg/g)
t (h)
100 ppm
60 ppm
40 ppm
20 ppm

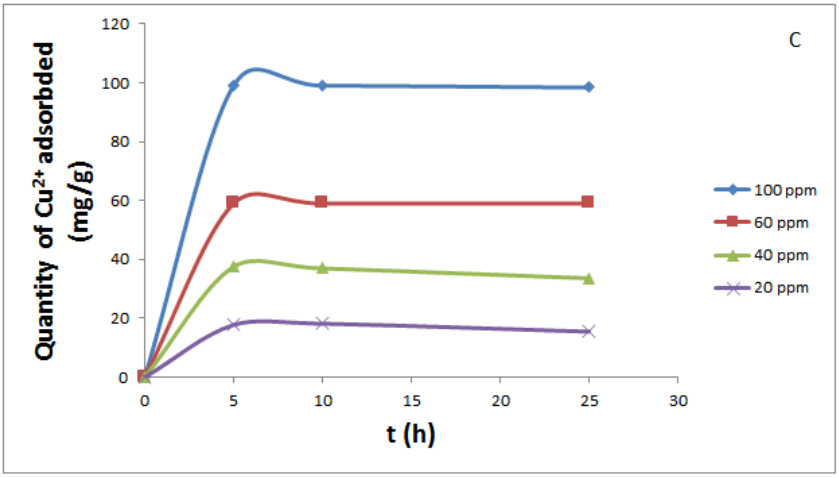

D
Quantity of Zn2+ adsorbded (mg/g)
t (h)
100 ppm
60 ppm
40 ppm
20 ppm

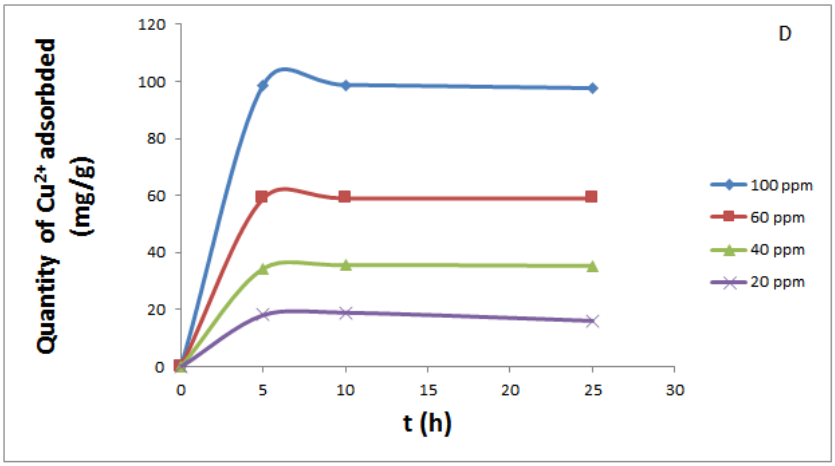
At pH -1, zinc ions are completely adsorbed by chitin after 5 hours of contact time at concentrations of 40 ppm (Figure 5.7 A). At higher values of pH, all zinc ions at different concentrations reached their adsorption equilibrium at 5 hours of contact time with chitin (Figure 5.7 B, C, and D). Based on these results, we can conclude that at 5 hours of contact time, the adsorbent surface is saturated by zinc metal ions.

5.5.1.2 Effect of contact time on adsorption behavior of copper 0 °C

Figure 5.8. Effect of contact time on the adsorption of copper ions at different initial concentrations and pH values. (A) pH 1, (B) pH 3, (C) pH 5, and (D) pH 7





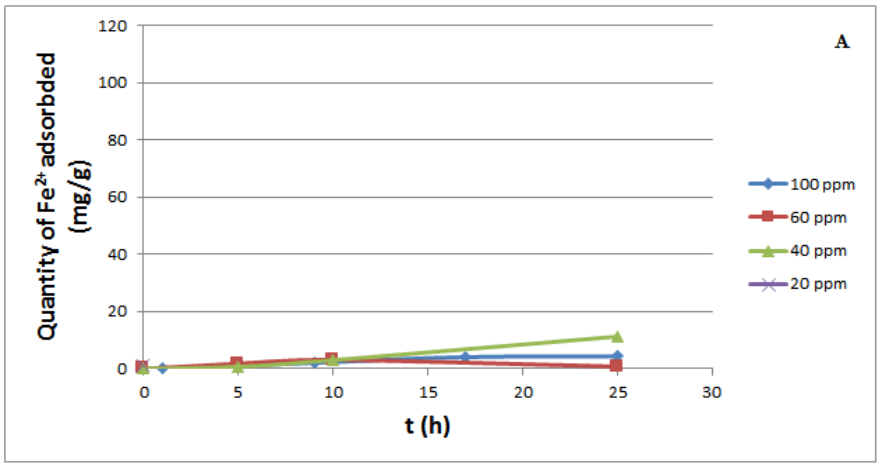


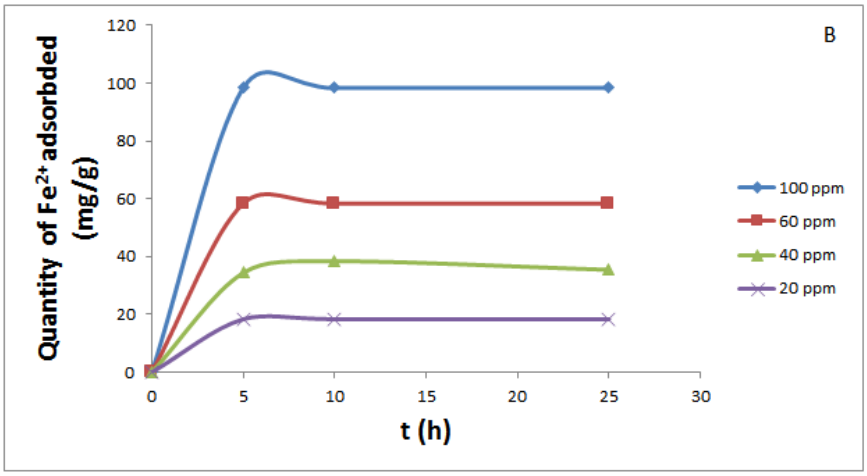
According to Figure 5.8 (A), in the highest concentrations of copper ions, 100 and 60 ppm, the amount of copper adsorbed by chitin reached its adsorption equilibrium at 10 hours, whereas the equilibrium, at 40 and 20 ppm, is not reached after 25 hours of contact time (Figure 5.8, A).

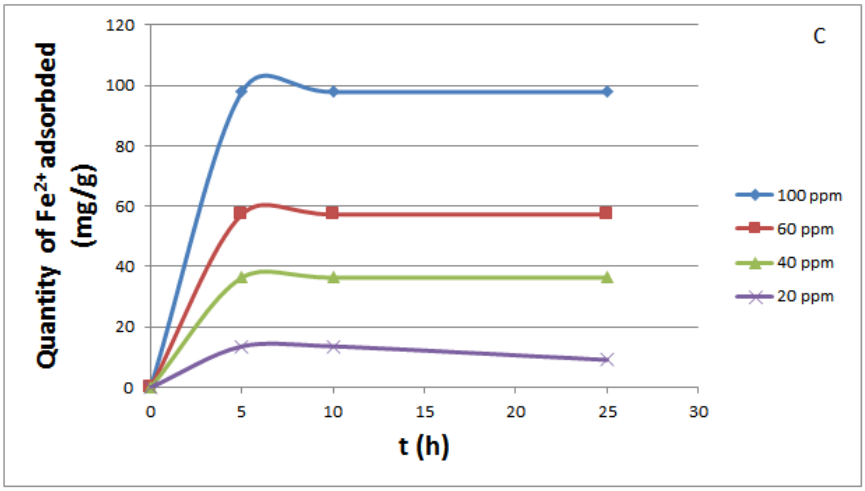
Additionally, when the pH of the solution increases from pH -3 to pH -7, we can observe that the amount of copper ions adsorbed by chitin reaches a plateau after 5 hours of contact time (Figure 5.8 B, C, and D). It is important to mention that, even though the adsorption equilibrium is not reached for some copper concentrations at pH -1 after 25 hours of contact time, higher pH values allow the complete adsorption of copper ions by chitin.

5.5.1.3 Effect of contact time on adsorption behavior for iron

Figure 5.9. Effect of contact time on the adsorption of iron ions at different initial concentrations and pH values. (A) pH 1, (B) pH 3, (C) pH 5, and (D) pH 7







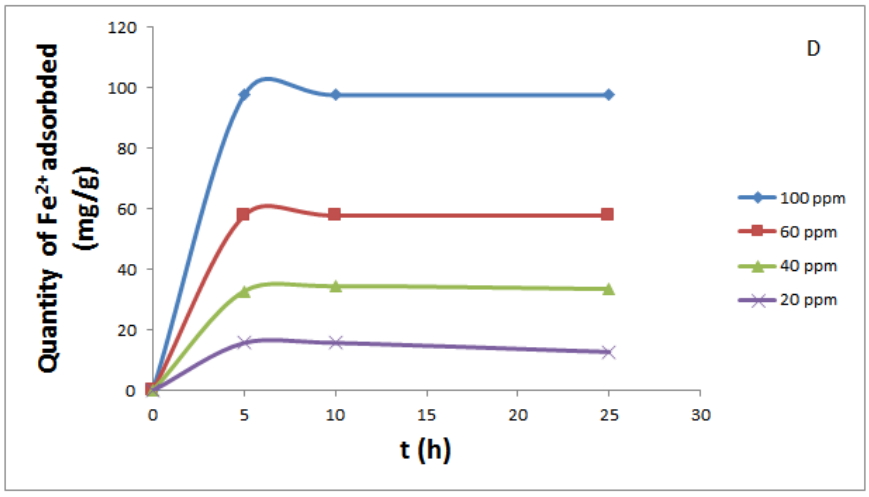
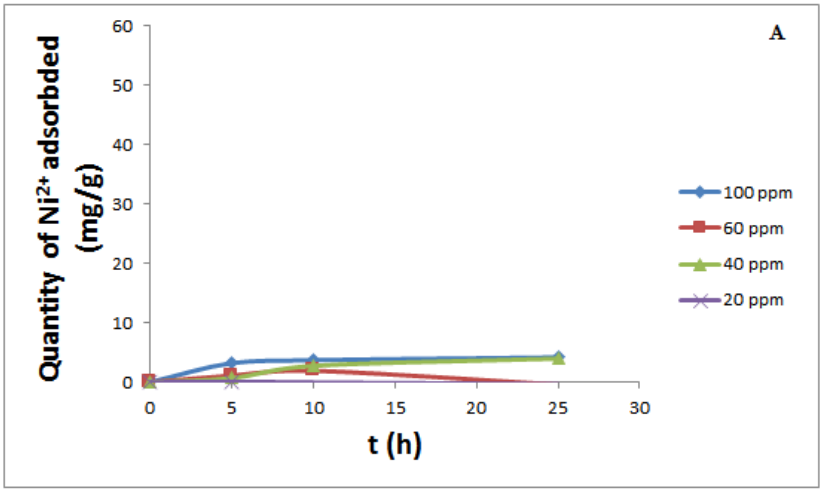
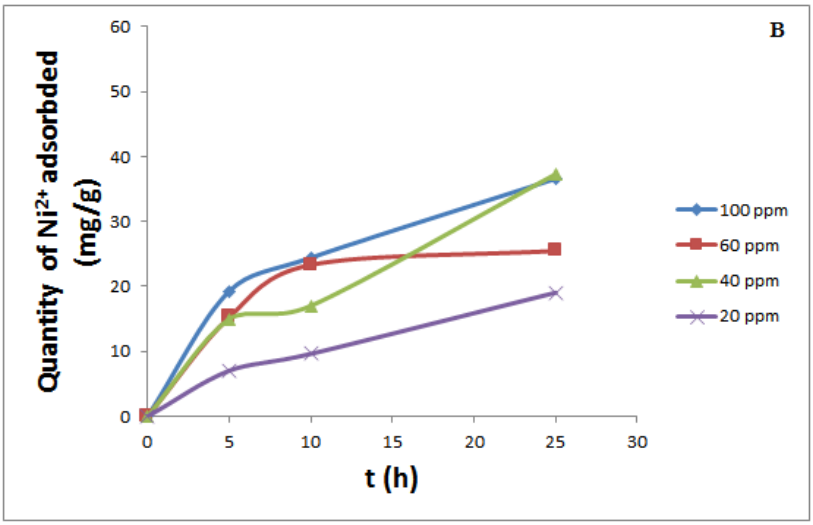


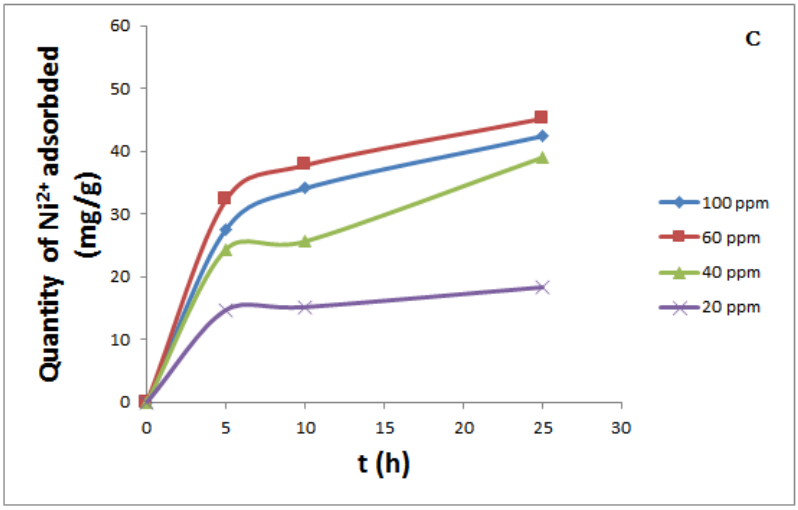
Figure 5.9 (A) shows that the adsorption equilibrium of iron ions by chitin is not completed after 25 hours of contact time at the initial concentration of 40 ppm. For the highest initial concentrations of iron, 100 and 60 ppm, the adsorption equilibrium of iron ions is reached at 17 and 10 hours, respectively (Figure 5.9 A); however, with increases in pH values from 3 to 7, iron ions reached their adsorption equilibrium at 5 hours in different initial concentrations (Figure 5.9 B, C, and D).

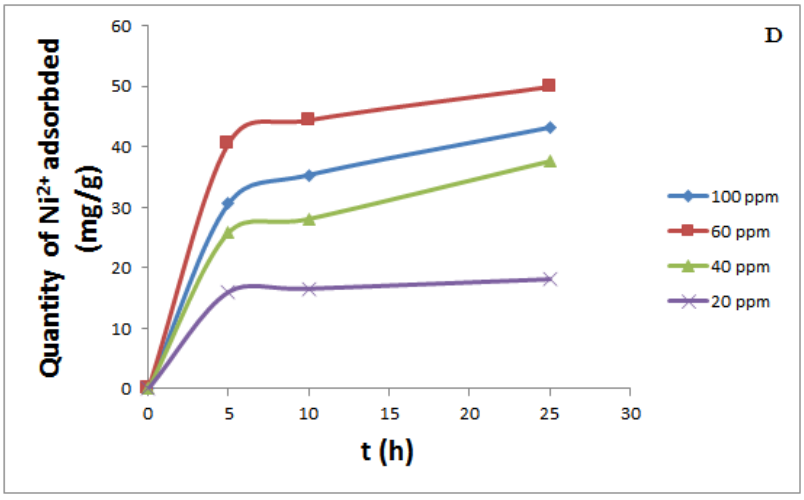
5.5.1.4 Effect of contact time on adsorption behavior for nickel

Figure 5.10. Effect of contact time on the adsorption of nickel ions at different initial concentrations and pH values. (A) pH 1, (B) pH 3, (C) pH 5, and (D) pH 7




B
Quantity of Ni2+ adsorbded (mg/g)
t (h)
100 ppm
60 ppm
40 ppm
20 ppm

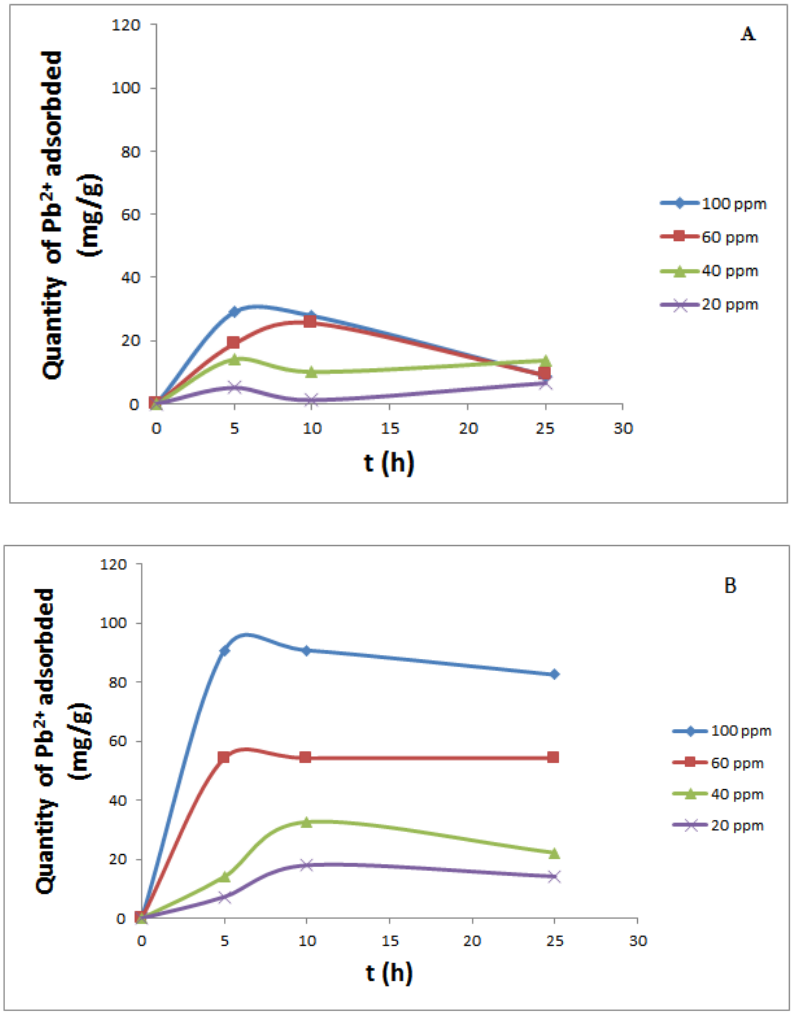

C
Quantity of Ni2+ adsorbded (mg/g)
t (h)
100 ppm
60 ppm
40 ppm
20 ppm

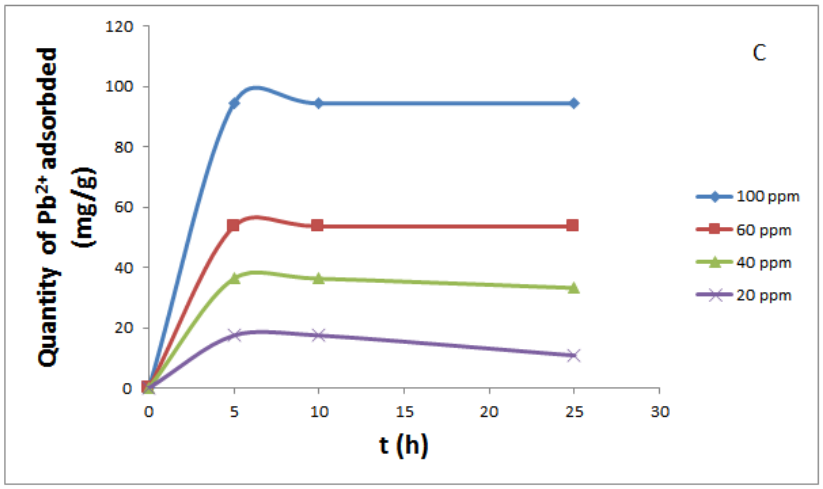

D
Quantity of Ni2+ adsorbded (mg/g)
t (h)
100 ppm
60 ppm
40 ppm
20 ppm

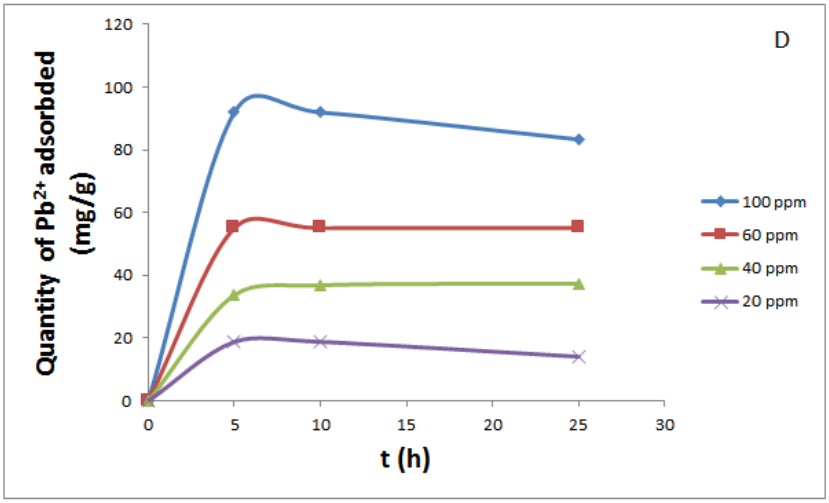
Based on the results of Figure 5.10 (A), we can conclude that the adsorption equilibrium is not achieved for nickel ions at the initial concentration of 100 ppm. Instead, at 60 and 40 ppm, nickel ions are mostly adsorbed after 10 hours, while the adsorption of nickel ions by chitin does not occur at the initial concentration of 20 ppm. Also, from Figure 5.10 (B), (C), and (D), we can observe that nickel ions are not completely adsorbed in concentrations from 100 to 40 ppm, except at the initial concentration of 20 ppm, where nickel ions are still being adsorbed after 25 hours

5.5.1.5 Effect of contact time on adsorption behavior for lead

Figure 5.11. Effect of contact time on the adsorption of lead ions at different initial concentrations and pH values. (A) pH 1, (B) pH 3, (C) pH 5, and (D) pH 7







From Figure 5.11 (A), (B), (C), and (D), we can observe that lead ions rapidly reached adsorption equilibrium after 5 hours of contact time at all values of pH for the different initial concentrations analyzed.

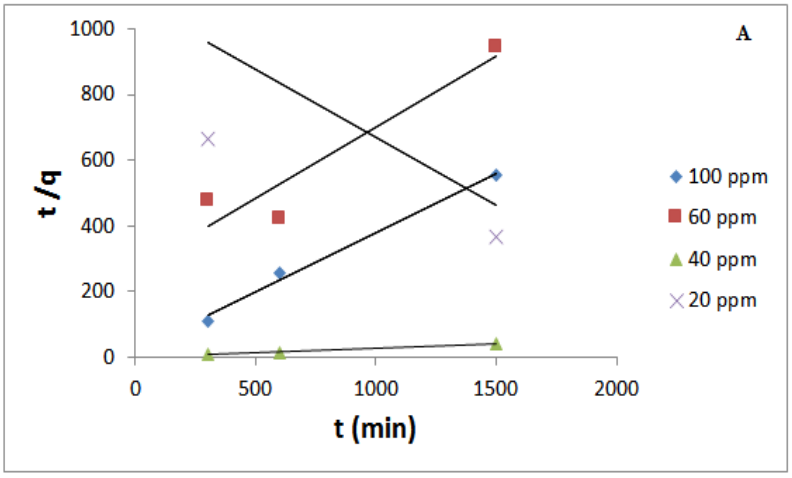
Consequently, from all the experiments performed to study the effect of contact time on the adsorption of metal ions by chitin, we can conclude that lead is the metal that presents more affinity to the sorbent compared with the other metals studied. Almost complete adsorption of lead by chitin can be observed after 5 hours of contact time at the different conditions analyzed.

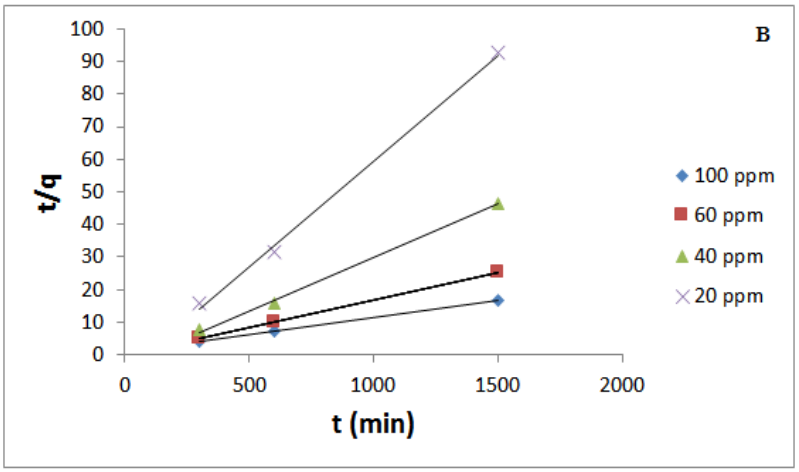
5.5.2 Pseudo second order kinetic analysis

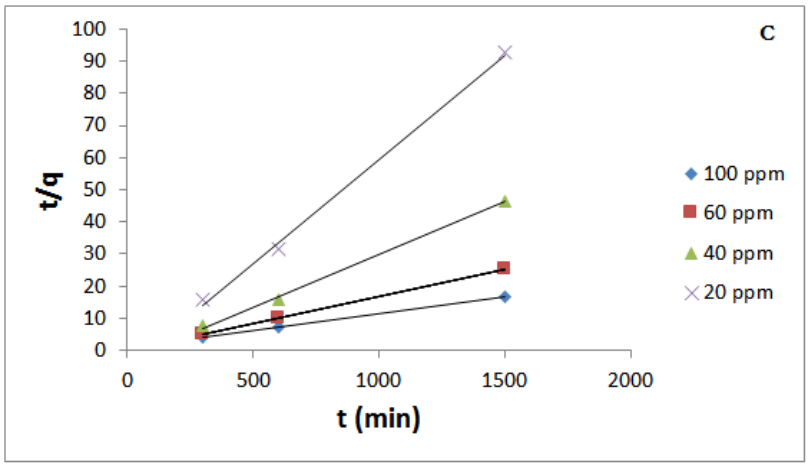
In order to analyse the adsorption kinetics of metals ions by chitin and to determine the kinetic the constant rate of each metal ion (K_2), the pseudo second order kinetic model is used. This model is known for fitting experimental batch adsorption studies at different times, and for estimating, reasonably well, kinetic parameters. The model is described in the fourth chapter.

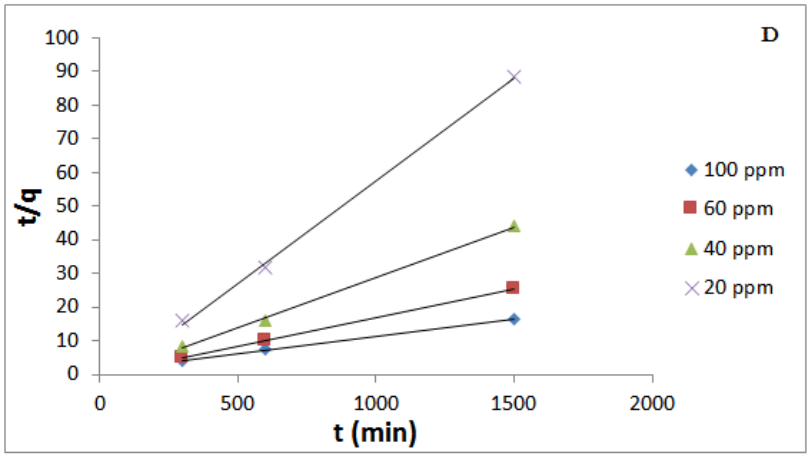
5.5.2.1 Pseudo second order kinetic analysis for zinc

Figure 5.12 Pseudo second order kinetics for zinc ions in concentrations from 20 to 100 ppm and different pH values. A) pH 1, B) pH 3, C) pH 5, D) pH 7.









According to Figure 5.12 and Appendix A, we can observe that the pseudo second order model fits the experimental data at pH-3, 5, and 7, showing straight lines with a high correlation coefficient (R^2) for zinc ions; however, at pH-1, for low concentrations of zinc ions, such as 20 ppm, the correlation coefficient R^2 is close to 0, which means that the model cannot explain the experimental data at 20 ppm. It is important to mention that the latter conclusion is confirmed by the contact time results, where at 20 ppm the uptake of zinc is less than 5 mg/g for the 25 hours studied.

The kinetic rate (K_2) can be determined using the intercept of the pseudo second order kinetic model (Linear form). The intercept (i) is defined as follows:

$$i = \frac{1}{K_2 . q_e^2}$$

Also, from the slope (s) of the pseudo second order kinetic model (Linear form), we can determine the equilibrium adsorption (q_e).The slope (s) is defined as:

$$q_e = \frac{1}{s}$$

Based on the results of Appendix A, we can also observe that, for most of the concentrations and pH values analyzed, the adsorption of zinc ions by chitin is a process that occurs rapidly.

Some other results, such as negative K_2 values may suggest that the adsorption behaviour between zinc ions and chitin is also affected by the acidic conditions of the system and the metal mixture analyzed; however, no literature is available to support the negative rates obtained from the pseudo second order model.

5.5.2.2 Pseudo second order kinetic analysis for copper

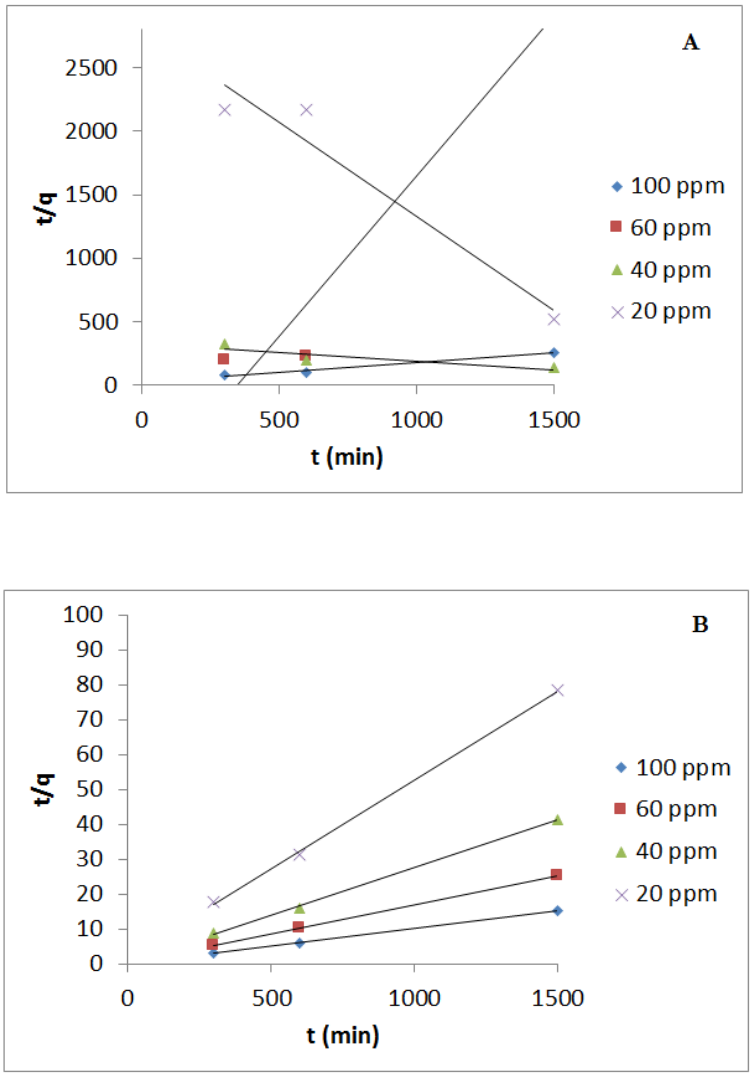
According to Figure 5.13 and Appendix B, we can observe that the pseudo second order kinetic model fits the experimental data, showing high correlation coefficients R^2 for most of the concentrations and pH values. It is important to note that for some results shown in Appendix B, where the rate is negative, we can conclude that the pseudo second order model does not fit the experimental data.

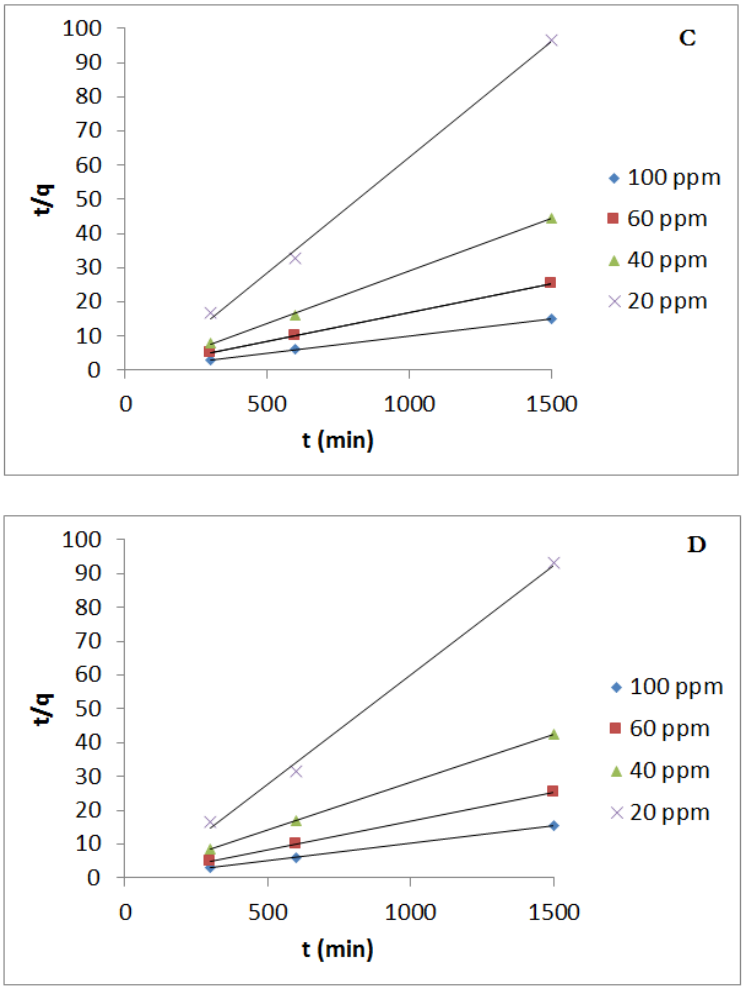
This fact, once again may be explained by the conditions of this study, where a mixture of 5 metals was analyzed. This conclusion suggests that further research needs to be performed

with different kinetics models, in order to fit and explain the adsorption behaviour of multicomponent systems.

Nevertheless, it is important to mention that, based on the contact time results for the different metals ions, the adsorption of copper is occurring and the adsorption equilibrium of copper ions is reached approximately after 5 hours of contact time with chitin.

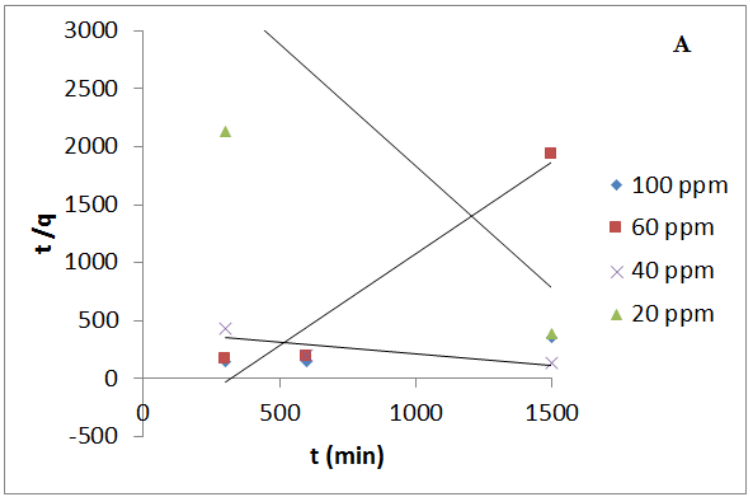
Figure 5.13. Pseudo second order kinetics for copper ions in concentrations from 20 to 100 ppm and different pH values. A) pH 1, B) pH 3, C) pH 5, D) pH 7.

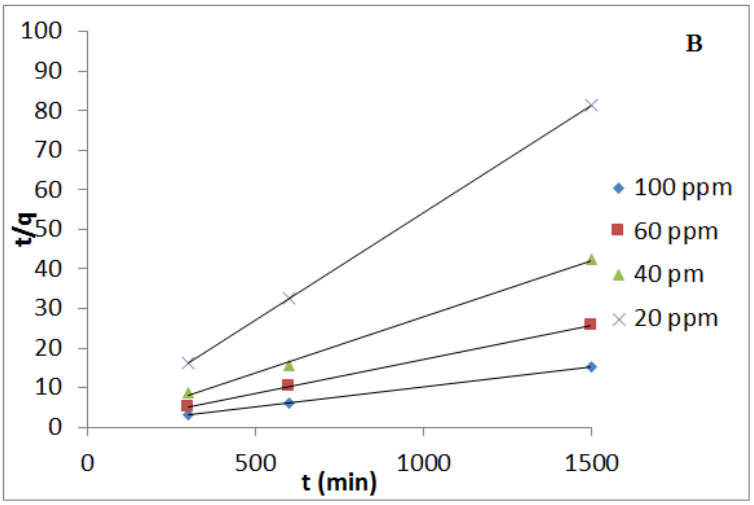


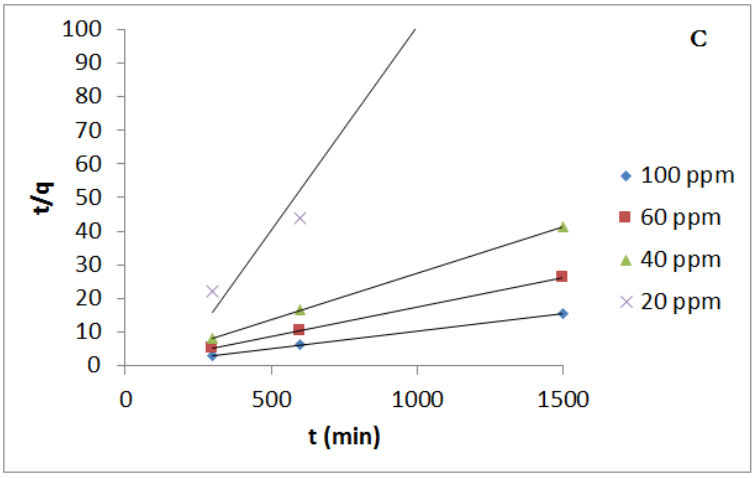


5.5.2.3 Pseudo second order kinetic analysis for iron

Figure 5.14: Pseudo second order kinetics for iron ions in concentrations from 20 to 100 ppm and different pH values. A) pH 1, B) pH 3, C) pH 5, D) pH 7.




B
t/q
t (min)
100 ppm
60 ppm
40 pm
20 ppm


C
t/q
t (min)
100 ppm
60 ppm
40 ppm
20 ppm

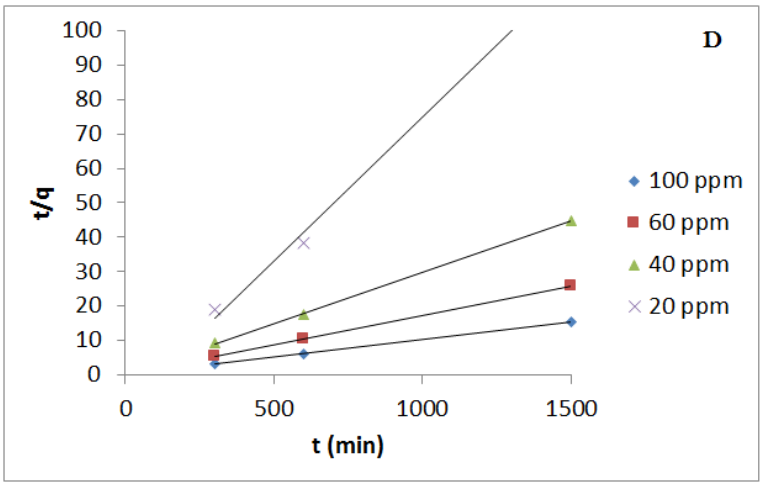

D
t/q
t (min)
100 ppm
60 ppm
40 ppm
20 ppm

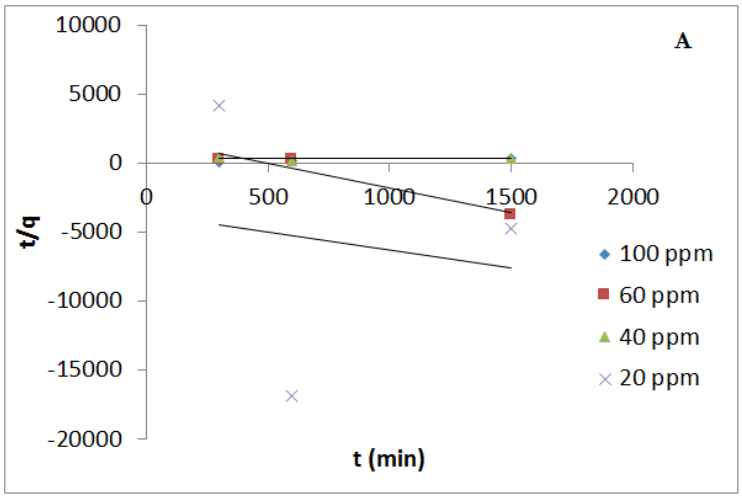
Figure 5.14 and Appendix C show that, at pH 1 and low concentrations of iron, 20 ppm and 40 ppm, the pseudo second order kinetic model does not properly fit the experimental data, giving low correlation coefficient values (R_2) of 0.4618 and 0.6884 respectively; however, at higher concentrations of iron, 60 ppm and 100 ppm, the correlation coefficient is close to 1, showing that the experimental data, at higher concentrations of iron and at pH 1, correlate with the pseudo second order kinetic model. Additionally, for some results shown in Appendix C, where the rate is negative, we can conclude that the pseudo second order model does not fit the experimental data. As mentioned before for zinc and copper, due to the complex systems analyzed, some adsorption behaviours cannot be explained with the use of the pseudo second order model and further research should be done in order to find the best mathematical model that explains a multicomponent system at 0 °C.

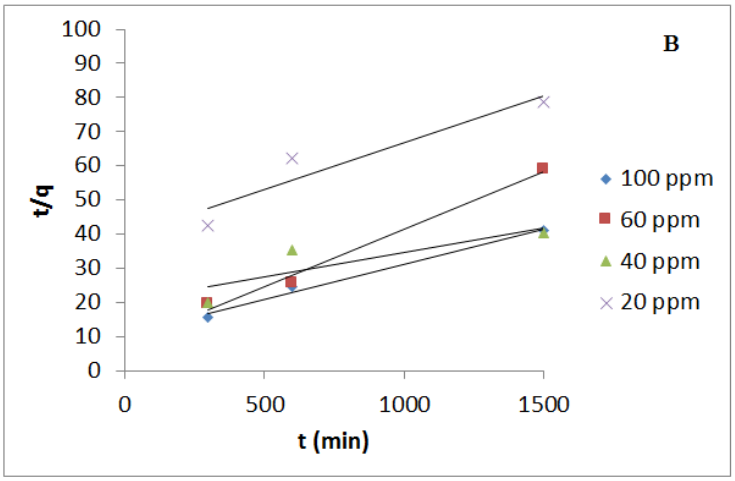
On the other hand, it is important to mention that, based on the contact time results of iron ions, we can conclude that the adsorption of copper is occurring and the adsorption equilibrium of copper ions is reached approximately after 5 hours of contact time with chitin.

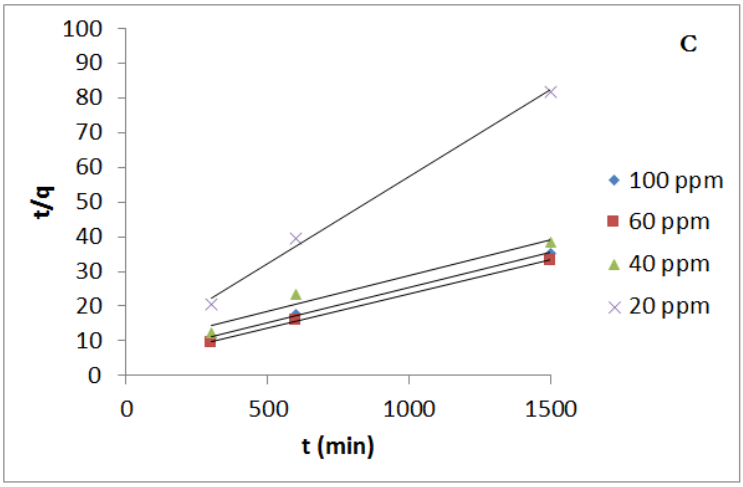
5.5.2.4 Pseudo second order kinetic analysis for nickel

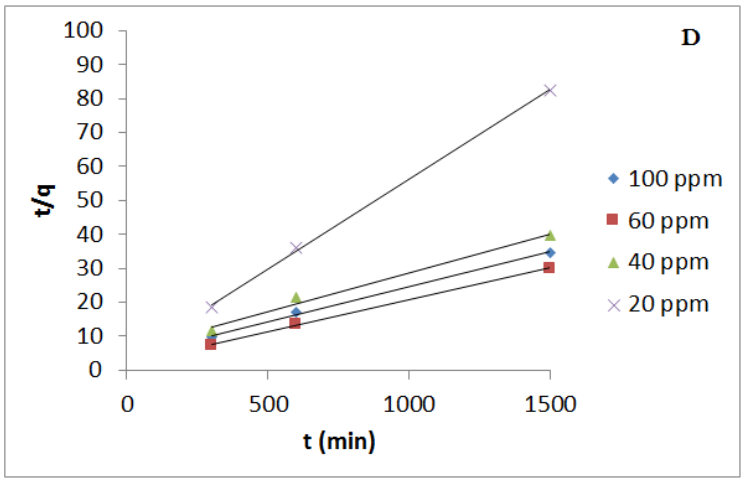
From Figure 5.15 and Appendix D, we can observe that all experimental data performed at pH-1 do not correlate with the pseudo second order model. The strong acidity of the solution and the complex system analyzed may not allow the analysis of the adsorption kinetics with this mathematical model; however, at pH- 3, 5, and 7, high correlation coefficients R, shows that the experimental data is explained by the kinetic model.

Figure 5.15: Pseudo second order kinetics for nickel ions from 20 ppm to 100 ppm at different pH. A) pH 1, B) pH 3, C) pH 5, D) pH 7.



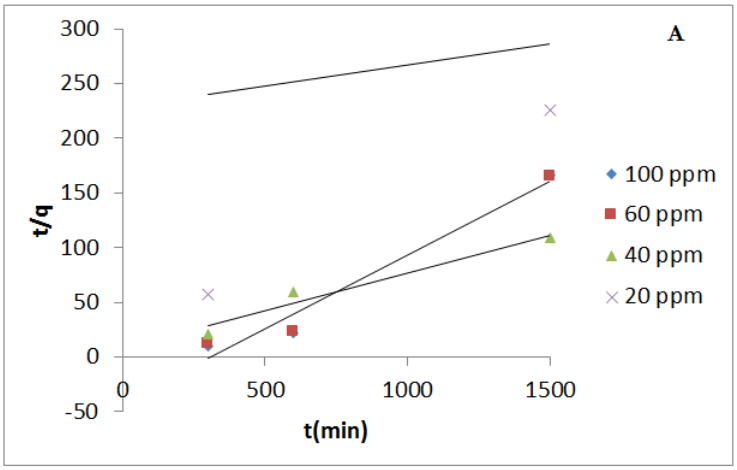


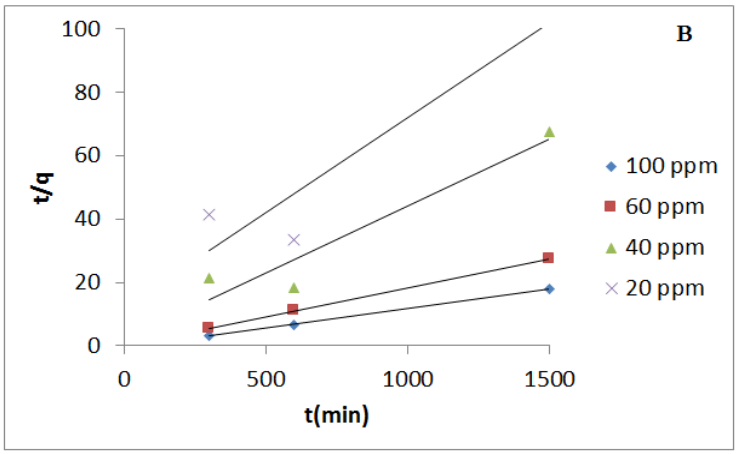


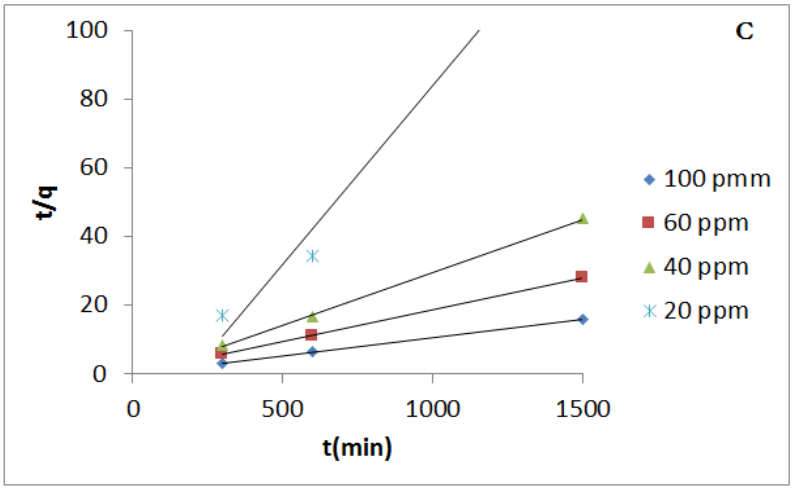


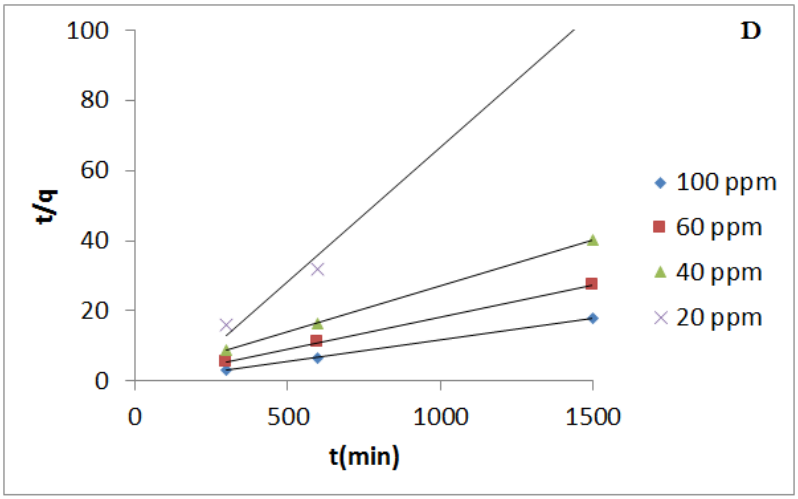
5.5.2.5 Pseudo second order kinetic analysis for lead

Figure 5.16: Pseudo second order kinetics for lead ions from 20 ppm to 100 ppm at different pH. A) pH 1, B) pH 3, C) pH 5, D) pH 7.









From Figure 5.16 and Appendix E, we can observe that the most of the experimental data is fitted by the pseudo second order kinetic model, with the exception of some results shown in Appendix E, where K_2 is negative. As mentioned before for the other metals analyzed, negative rates may suggest that the adsorption behaviour between lead ions and chitin is affected by the acidic conditions of the system and the metal mixture analyzed; however, based on the contact time results for the lead ions, the adsorption of lead is occurring and the adsorption equilibrium of lead ions is reached approximately after 5 hours of contact time with chitin.

Chapter 6

6. Conclusions and discussion

Extensive literature can be found regarding wastewater treatment by using methods, such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, ion exchange, reverse osmosis, filtration, evaporation recovery, and electrocoagulation; however, all these methods have their own disadvantages. Some of the disadvantages include high energy requirements, the inefficient recovery of pollutants, the generation of toxic sludge, and expensive equipment. Thus, the need to improve or develop new methods has become the major priority to treat wastewater. Adsorption, a relatively new method, has proved to be rapid, cost efficient, and environmentally friendly compared with other methods [77].

Also, according to Desta in her article, "Batch Sorption Experiments: Langmuir and Freundlich Isotherm Studies for the Adsorption of Textile Metal Ions onto Teff Straw (Eragrostis tef) Agricultural Waste," the most common adsorbent used to remove heavy metals is activated carbon [77]; however, some other adsorbents, such as chitin and chitosan, have proved to be efficient and cost-effective in the recovery of heavy metals from aqueous solutions [60, 61], and based on the results of the tests performed at room temperature and at 0 °C, we can confirm that chitin has good affinity for Pb, Fe, Ni, Cu, and Zn [77].

It is important to mention that because of the complex nature of the adsorption systems using a mixture of components, "there is no specific model that can universally be applied [to every system] [65]," and as a consequence, the model analyzed could not be fitted to the Langmuir or Freundlich isotherm.

It is important to conclude that due to the fact that effluents from industries, such as mining, metal processing, finishing, and plating, contain several soluble heavy metals, a metal mixture is used in this study in order to simulate real conditions. Thus, due to the complex system analyzed, Langmuir and Freundlich isotherm models, for individual systems, could not be fitted to the experimental data, and as a consequence, multicomponent system isotherms cannot be applied due to the assumptions of each model (Langmuir and Freundlich).

According to Gerente *et al.*, in their article, "Application of chitosan for the removal of metals From wastewaters by adsorption—mechanisms and models review," "the apparent lack of comparisons of the results with other isotherm equations is a significant problem for potential future applications of existing chitosan results to the design of multicomponent metal ion containing wastewaters [64]." Thus, the application of isotherm models, such as Langmuir and Freundlich isotherms, for multicomponent systems "can no longer be justified and other isotherms should be analyzed for comparison [64]."

Based on the results analyzed in the fifth chapter, we can conclude that the adsorption of heavy metals ions at room temperature is absolutely possible, especially for iron, lead and copper at pH 3, 5, and 7, and at 0 °C for iron, lead, copper and zinc at pH 3, 5, and 7. Thus, we can state that chitin could be used to treat wastewater present in discharge points from mining facilities in Newfoundland and Labrador; however, research needs to be done in order to confirm the maximum uptake of the adsorbent for the different heavy metal ions.

The uptake of heavy metals by lobster biomass was analyzed varying parameters, such as the temperature, pH, and concentration through batch experiments. The results of the batch tests

show that lobster biomass has the following descending order of preference for adsorption of the different metallic ions: Pb > Fe > Zn > Cu > Ni at 0 °C. At room temperature, the results show that the descending order of preference is: Pb > Fe > Zn > Cu.

It is important to mention that nickel is the metal with the lowest % adsorption, at room temperature and at 0 °C, among all the metals analyzed in this study. Also, it is important to mention that, with the exception of lead, the pH appears to be the most influencing factor of the adsorption process, and as a consequence, the % adsorption of all metal ions is considerably affected at pH-1. In general, increments of pH values benefit the adsorption removal of cationic metals. For all the metal ions analyzed in this study, Zn(II), Cu(II), Fe(II), Ni(II), and Pb(II), a large improvement in the adsorption capacity of metal ions was observed with increments in pH.

Also, it is important to note that, at room temperature and 0 °C, the % adsorption is affected by the solution's concentration. For instance, nickel and zinc at room temperature show that the % adsorption increases at lower solute concentrations. This can be explained by the number of available sites on the surface of the lobster biomass to bind metallic ions. At high concentrations, such as 60 and 100 ppm, the % adsorption is lower than 40% for zinc and nickel as a consequence of the adsorbent's saturation, whereas in concentrations of 20 ppm the % adsorption considerably increases to 50 and 100% for nickel and zinc respectively. On the other hand, at 0 °C, the % adsorption of nickel ranges from 40% at 100 ppm to 70% at 20 ppm. Thus, we can conclude that, for zinc and nickel at room temperature, and for nickel 0 °C, the percentage adsorption increases as a result of a lower concentration of metalic ions in the solution compared with the number of available sites in the adsorbent.

Additionally, based on the results analyzed in the fifth chapter, we can confirm that temperature seem to affect the adsorption uptake to a lesser extent [3]. This can be confirmed by the results of zinc and nickel that, for most of the adsorption values at different concentrations and pH values, with the exception of pH-1, the recovery is higher at 0 °C than at room temperature; however, it is important to mention that no test has been performed until now trying to analyze the adsorption of metallic ions in aqueous solutions at 0 °C, and as a consequence, no literature is available that supports these results. Thus, research needs to be done in order to confirm that the % adsorption of some metals is higher at 0 °C than at room temperature.

According to Volesky, "the best results of a sorption system come from the equilibrium sorption studies [5]." In other words, enough time needs to pass in order to reach the equilibrium between the adsorbent and the sorbate in the solution. Thus, based on the kinetic analysis, we can conclude that for all the metals studied at most of the concentrations and pH values, the adsorption equilibrium is reached after 5 hours of contact time.

It is also important to mention that the recovery of loaded pollutants was not tested on the resultant lobster's shell powder. One bio-sorbent is considered to be useful if it has good bio-sorptive capacity but also if desorption can be easily applied by a simple and non-destructive physical/chemical method [3]. In other words, the bio-sorptive capacity and the feasibility to regenerate and reuse the bio-sorbent are two significant characteristics that need to be tested in order to consider the bio-sorbent suitable for treating wastewater in discharge points from mining facilities in Newfoundland and Labrador.

Finally, further research needs to be done in order to find the maximum equilibrium of each metal in a mixture of metals, to confirm the effect of the temperature in the uptake of metal ions from aqueous solutions, to analyze changes of pH during the course of an adsorption experiment, and to prove the same results using real water from the discharge points of mining facilities in Newfoundland and Labrador, due to the fact that the one used in the tests was synthetic wastewater.

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Appendices

Appendix A

Pseudo second order kinetic parameters for zinc ions.

	C_0 (ppm)	qe (ppm)	K ($g/mg^{-1}.min^{-1}$)	R^2
Ph1	100 ppm	1.3523	6.35E-03	0.9621
	60 ppm	1.285	1.59E-03	0.6644
	40 ppm	176.37	6.72E-06	0.9227
	20 ppm	-2.006	2.76E-04	0.118
Ph3	100 ppm	49.261	9.57E-05	0.9526
	60 ppm	31.153	2.22E-04	0.9306
	40 ppm	19.455	4.10E-04	0.9013
	20 ppm	9.9404	7.86E-04	0.9023
Ph5	100 ppm	94.34	1.25E-04	0.9995
	60 ppm	58.824	4.82E+10	0.9999
	40 ppm	30.488	-3.74E-04	0.9982
	20 ppm	15.408	-7.95E-04	0.9978
Ph7	100 ppm	97.087	1.04E-04	0.9997
	60 ppm	59.172	-2.86E+10	0.9999
	40 ppm	33.333	-7.93E-04	0.9989
	20 ppm	16.367	-1.07E-03	0.9989

Appendix B

Pseudo second order kinetic parameters for copper ions.

	C_0 (ppm)	qe (ppm)	K ($g/mg^{-1}.min^{-1}$)	R^2
Ph1	100	6.33714	1.08E-03	0.9889
	60	0.39741	-7.33E-03	0.9467
	40	-7.2254	1.57E-01	0.7844
	20	-0.6761	1.63E-04	0.9423
Ph3	100	99.0099	1.77E-03	0.9999
	60	59.1716	4.76E+10	0.9999
	40	36.63	3.64E-03	0.9983
	20	19.6078	1.50E-03	0.9993
Ph5	100	98.0392	-2.76E-03	0.9999
	60	58.8235	1.00E-02	0.9999
	40	32.4675	-5.72E-04	0,9993
	20	14.7929	-8.77E-04	0.9974
Ph7	100	97.0874	-1.58E-03	0.9999
	60	58.8235	1.00E-02	0.9999
	40	35.5872	4.97E-02	0.9999
	20	15.4321	-8.89E-04	0.9969

Appendix C

Pseudo second order kinetic parameters for iron ions.

	C_0 (ppm)	qe (ppm)	K ($g/mg^{-1}.min^{-1}$)	R^2
Ph1	100	0.63231	-5.00E-03	0.9485
	60	0.63231	-5.00E-03	0.9485
	40	-4.8263	1.02E-04	0.6884
	20	-0.4743	1.13E-03	0.4618
Ph3	100	98.0392	1.04E-01	0.9999
	60	58.4795	2.92E-01	0.9999
	40	35.2113	-1.70E-03	0.9978
	20	18.4162	9.83E+10	0.9999
Ph5	100	98.0392	3.47E+10	0.9999
	60	57.1429	3.06E-01	0.9999
	40	36.3636	7.56E-01	0.9999
	20	8.21693	-7.16E-04	0.9905
Ph7	100	98.0392	1.73E+10	0.9999
	60	57.8035	2.99E-01	0.9999
	40	33.557	-9.77E-03	0.09997
	20	11.9332	-8.11E-04	0.9965

Appendix D

Pseudo second order kinetic parameters for nickel ions.

	C_0 (ppm)	qe (ppm)	K ($g/mg^{-1}.min^{-1}$)	R^2
Ph1	100	-133.33	1.58E-07	0.0015
	60	-0.2757	7.15E-03	0.9377
	40	-133.33	1.58E-07	0.0015
	20	-0.3873	-1.80E-03	0.0232
Ph3	100	48.7805	3.95E-05	0.9871
	60	29.7619	1.44E-04	0.9903
	40	70.4225	9.86E-06	0.7133
	20	36.4964	1.91E-05	0.8933
Ph5	100	49.505	8.01E-05	0.9993
	60	50.7614	1.06E-04	0.9992
	40	48.5437	5.15E-05	0.9629
	20	19.9203	3.55E-04	0.9955
Ph7	100	48.7805	1.03E-04	0.9984
	60	53.4759	1.77E-04	0.9995
	40	43.8596	8.67E-05	0.9893
	20	18.9036	7.85E-04	0.9993

Appendix E

Pseudo second order kinetic parameters for lead ions.

	C_0 (ppm)	qe (ppm)	K ($g/mg^{-1}.min^{-1}$)	R^2
Ph1	100	7.4184	-4.34E-04	0.97
	60	7.4184	-4.34E-04	0.97
	40	14.4718	6.12E-04	0.959
	20	25.7732	6.60E-06	0.0121
Ph3	100	80	-2.46E-04	0.9991
	60	54.3478	3.39E-01	0.9999
	40	23.6407	9.38E-04	0.915
	20	16.7224	2.92E-04	0.8869
Ph5	100	94.3396	1.12E-01	0.9999
	60	53.7634	3.46E-01	0.9999
	40	32.2581	-6.51E-04	0.9992
	20	9.57854	-5.39E-04	0.9877
Ph7	100	80.6452	-2.37E-04	0.9991
	60	54.9451	-5.52E+10	0.9999
	40	38.3142	7.94E-04	0.9998
	20	13.0039	-5.79E-04	0.9942